

High-valent Nickel Complexes Supported by Pyridinedicarboxamidate Ligands in Hydrocarbon Oxidation Reactions

A thesis submitted to to the University of Dublin in fulfilment of the
requirements for the degree of Doctor of Philosophy by

Paolo Pirovano

Under the supervision of Dr A. R. McDonald

School of Chemistry
Trinity College Dublin
2017

I declare that this thesis has not been submitted as an exercise for a degree at this or any other university and is my own work. Parts of the work described herein are the product of collaboration and are acknowledged at the beginning of each chapter. I agree to deposit this thesis in the University's open access institutional repository or allow the library to so on my behalf, subject to Irish Copyright legislation and Trinity College Library conditions of use and acknowledgements.

.....

Paolo Pirovano

Summary

High-valent M=O and M–O–X complexes are hypothesised to be potent oxidising intermediates both in enzymatic and small-molecule catalysis. In contrast to those from groups 6-8, oxidants that contain late transition metals (Co, Ni, Cu) are poorly understood. The main topics of the work described in this thesis are the preparation, characterisation and study of the oxidative reactivity of high-valent nickel complexes, supported by pyridinedicarboxamidate ligands ($\text{pyN}_2^{\text{Me}_2}$ and $\text{pyN}_2^{i\text{Pr}_2}$). In chapter 2, the initial discovery that the complex $[\text{Ni}^{\text{II}}(\text{OCO}_2\text{H})(\text{pyN}_2^{\text{Me}_2})]^-$ could be reacted at low temperature ($<-40\text{ }^\circ\text{C}$) with a one electron chemical oxidant (tris(4-bromophenyl)ammoniumyl hexachloroantimonate – magic blue), to form the metastable $[\text{Ni}^{\text{III}}(\text{OCO}_2\text{H})(\text{pyN}_2^{\text{Me}_2})]$ is described. This species was characterised by EPR and XAS spectroscopies, and DFT calculations, confirming its identity as a Ni^{III} complex. It was shown that it was competent in the oxidation of several substrates, including those with weak O–H bonds (2,6-di-*tert*-butylphenol) and C–H bonds (1-benzyl-1,4-dihydronicotinamide). A D/H kinetic isotope effect of 2.1, in the oxidation of 2,6-DTBP, hinted towards an hydrogen atom transfer or proton-coupled electron transfer type mechanism.

In successive work, the scope of the investigation was extended by substituting the $^-\text{OCO}_2\text{H}$ ligand with other monodentate O donors (^-OAc and $^-\text{ONO}_2$; chapter 3) and multidentate N/O ligands (*acac*, *bpy*, *terpy*, 2,6-dipicolinate; chapter 4). This involved the development of a widely applicable synthetic method, consisting in the displacement of the acetonitrile in $[\text{Ni}^{\text{II}}(\text{CH}_3\text{CN})(\text{pyN}_2^{\text{Me}_2})]$ by the desired ligand. All resulting Ni^{II} compounds were characterised by X-ray diffraction, and NMR, MS and FTIR spectroscopies.

Through methods analogous to those employed for the $\text{Ni}^{\text{III}}\text{--OCO}_2\text{H}$ compound, that is, oxidation of the Ni^{II} complexes with either magic blue, cerium ammonium nitrate or hypochlorous acid, several more Ni^{III} oxidants were prepared and characterised. Analysis of their reactivity in the oxidation of phenols demonstrated that electron poor species, *i.e.* those with weakly basic ligands, and in particular the $\text{Ni}^{\text{III}}\text{--ONO}_2$ complex, were the best oxidants, with the highest reaction rates. The $\text{Ni}^{\text{III}}\text{--OAc}$ complex was moderately stable at $25\text{ }^\circ\text{C}$, allowing extensive study of its reactivity with hydrocarbons. It oxidised a wide range of hydrocarbons, with $\text{BDE}_{\text{C-H}}$ values going from 75.5 (xanthene) to 89 kcal/mol (toluene). Kinetic analysis revealed a linear relation between reaction rates and the $\text{BDE}_{\text{C-H}}$ of the substrates (Bell-Evans-Polanyi relationship); together with observed KIEs of 3.0-3.3, this constituted strong evidence of an hydrogen atom transfer mechanism. Importantly, the reaction rates were particularly high, surpassing those of most known $\text{Mn}^{\text{III}}\text{--O--X}$ and $\text{Fe}^{\text{III}}\text{--O--X}$ oxidants, and rivalling $\text{Fe}^{\text{IV}}\text{=O}$ and $\text{Cu}^{\text{III}}\text{--OH}$ species which are amongst

the fastest known hydrogen atom abstractors. High valent nickel-oxygen complexes, and complexes of the late transition metals in general, look thus to be quite powerful oxidants.

Unlike these $\text{Ni}^{\text{III}}\text{--O--X}$ compounds, neither species with the Ni^{IV} oxidation state, nor having an oxo ligand, had sufficient stability to be spectroscopically observed, even at low temperatures ($\leq -80\text{ }^{\circ}\text{C}$). Nevertheless, in chapter 5, evidence that a highly reactive intermediate is transiently formed in the reaction of $[\text{Ni}^{\text{II}}(\text{CH}_3\text{CN})(\text{pyN}_2^{i\text{Pr}_2})]$ with *m*-CPBA is shown. Through the analysis of decay products, isotopic labelling experiments and DFT calculations it was determined that in this reaction *m*-CPBA acted as a two-electron oxidant, forming a $\text{Ni}^{\text{III}}\text{--O}^{\bullet}$ species, $[\text{Ni}^{\text{III}}(\text{O}^{\bullet})(\text{pyN}_2^{i\text{Pr}_2})]$. Interestingly, the principal decay pathway of this intermediate involved hydrogen atom abstraction from a benzylic C–H group of the supporting ligand, which after radical rebound and cyclisation of the resulting benzyl alcohol, led to the formation of an unusual benzoxazine product.

In the last chapter of the thesis (chapter 6) the coordination of $\text{pyN}_2^{i\text{Pr}_2}$ ligand to other metals, specifically cobalt and zinc, is explored. A Co^{II} complex, $[\text{Co}^{\text{II}}(\text{CH}_3\text{CN})(\text{pyN}_2^{i\text{Pr}_2})]$, was synthesised, which interestingly was isostructural to $[\text{Ni}^{\text{II}}(\text{CH}_3\text{CN})(\text{pyN}_2^{i\text{Pr}_2})]$. In view of employing it as a precursor to high-valent oxidants, the introduction of an O-donor ligand (^-OAc) was tested: while not structurally characterised, ^1H NMR and UV-Vis spectroscopies demonstrated the formation of a new species, presumably $\text{Co}^{\text{II}}\text{--OAc}$. The oxidation of $[\text{Co}^{\text{II}}(\text{CH}_3\text{CN})(\text{pyN}_2^{i\text{Pr}_2})]$, and its ^-OAc adduct were also assessed in cyclic voltammetry experiments. Complexes $[\text{Zn}^{\text{II}}(\text{OAc})(\text{pyN}_2^{i\text{Pr}_2})]^-$ and $[\text{Zn}^{\text{II}}(\text{Br})_2(\text{HpyN}_2^{i\text{Pr}_2})]^-$ were also formed, and a crystal structure of the dibromozinc species was obtained, which revealed a tetrahedral zinc centre, with one of the amide groups of $\text{pyN}_2^{i\text{Pr}_2}$ protonated and not involved in binding to the metal.

Acknowledgements

I would like to express my appreciation for all the people who have given assistance, encouragement and support during the last four years. My first thanks are for my advisor, Dr Aidan McDonald, for his teaching, guidance and providing motivation throughout this work. I'm also grateful for the opportunities he has offered me towards my growth as a scientist.

I want to thank to all the collaborators have contributed to this project: A. J. Fitzpatrick and Prof. Grace G. Morgan (UCD) for providing access to the Magnetech Miniscope EPR spectrometer and helping with the data collection; Prof Robert Barklie (School of Physics, TCD) for access and training to the Bruker EMX EPR spectrometer; Dr Appu Draksharapu and Prof. Wesley Browne (University of Groningen) for resonance Raman measurements; Prof. Marcel Swart (University of Girona) for the DFT calculations and Dr Eric R. Farquhar (Brookhaven National Laboratory) for X-Ray absorption spectroscopy. I'm grateful to the ECOSTBio action for giving me the chance to present this work at ICC2016 and supporting travel.

The technical staff in the school of Chemistry has also been extremely helpful: special thanks go to Dr Brendan Twamley who has done X-ray diffraction data collection, solution and refinement for all the crystal structures published in this thesis. I thank Dr Martin Feeney and Dr Gary Hessman for the measurement of mass spectra, and Dr John O'Brien and Dr Manuel Rueher who have aided with NMR spectroscopic measurements.

Finally, I want to acknowledge the undergraduate students who I have supervised and have done preliminary work on the projects directly related to this thesis, Iain Fisher, Jack Kiernan, Chiara Cecchini, and Abigail Berry.

The present and past members of the McDonald group, Andy, Xin, Adriana, Ciara, Jackie, Peppe, Marta, Bertrand, Ankita, Prasenjit and Philipp have all contributed to make the research a success and have made these four years in Dublin enjoyable (especially at Oktoberfest!). Andy was the first person I met in the group and he has been a valid friend, and in keeping the lab alive and discussing chemistry; he has also helped reading over part of this thesis. Peppe and Marta, who would have predicted that one day I wouldn't hate you any more!

I also want to thank all my other friends in the department, the Italian crowd has been great fun and have almost helped me stay sane in the last year. Maybe I'll say hi next time we meet in the corridors. Cecilia, since we unknowingly showed up in Dublin at the same time four years ago, it's been an adventure going through our parallel PhDs. We'll soon win it out! Thanks to Dani, who has been there when things were going great and in the difficult moments, and whose support was invaluable.

Finally, a special thanks to my family back home, for everything they have done for me and the support they have shown.

Abbreviations

<i>acac</i>	acetylacetonate(–)
ATR-FTIR	attenuated total reflectance - Fourier transform infrared
BDE	bond dissociation energy
BDFE	bond dissociation free energy
Bn-TPEN	<i>N</i> -benzyl- <i>N,N',N'</i> -tris(2-pyridylmethyl)-1,2-diaminoethane
BNAH	1-benzyl-1,4-dihydronicotinamide
BPMCN	<i>N,N'</i> -bis(2-pyridylmethyl)- <i>N,N'</i> -dimethyl- <i>trans</i> -cyclohexane-1,2-diamine
<i>bpy</i>	2,2'-bipyridine
H ₃ buea	tris((<i>N</i> 9- <i>tert</i> -butylureaylato)- <i>N</i> -ethyl))aminato(3–)
H ₃ bupa	bis((<i>N'</i> - <i>tert</i> -butylureayl)- <i>N</i> -ethyl)-(6-pivalamido-2-pyridylmethyl)-amine(2–)
BVS	bond valence sum
CAN	cerium(IV) ammonium nitrate
CPET	concerted proton-electron transfer
ctb	<i>N,N,N',N'</i> -tetrakis((benzoimidazol-2-yl)methyl)cyclohexane- <i>trans</i> -1,2-diamine
DFT	density functional theory
DHA	9,10-dihydroanthracene
2,6- <i>dipic</i>	2,6-pyridinedicarboxylate
DMF	dimethylformamide
DMSO	dimethylsulfoxide
dpaq ^{2Me}	2-(bis(pyridin-2-ylmethyl))amino- <i>N</i> -2-methylquinolin-8-yl-acetamidato(–)
dpaq ^H	2-(bis(pyridin-2-ylmethyl))amino- <i>N</i> -quinolin-8-yl-acetamidato(–)
DTBP	2,6-di- <i>tert</i> -butylphenol
EPR	electron paramagnetic resonance
ET–PT	electron transfer - proton transfer
EXAFS	extended X-ray absorption fine structure
Fc	ferrocene
FWHM	full width at half maximum

GC-MS	gas chromatography - mass spectrometry
GOF	goodness of fit
HAA	hydrogen atom abstraction
HAT	hydrogen atom transfer
KIE	kinetic isotope effect
LA	Lewis acid
<i>m</i> -CPBA	<i>m</i> -chloroperbenzoic acid
magic blue	tris(4-bromophenyl)ammoniumyl hexachloroantimonate
Me ₂ EBC	4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane
Mes	mesityl, 2,4,6-trimethylphenyl
^{Mes} salen	5',5'''-(((1,2-dimesitylethane-1,2-diyl)bis(azanylylidene)))bis(methanylylidene))bis(2,2'',4,4'',6,6'' hexamethyl-[1,1':3',1''-terphenyl]-4'-olate)(2-)
MST	<i>N,N,N'</i> -[2,2',2''-nitrilotris(ethane-2,1-diyl)]tris(2,4,6-trimethylbenzene)-sulfonamidato(3-)
μ_B	Bohr magneton
N4py	1,1-di(pyridin-2-yl)- <i>N,N</i> -bis(pyridin-2-ylmethyl)-methanamine
NIR	near infrared
NO ₂ pyN ₂ ^{<i>i</i>Pr₂}	<i>N,N'</i> -bis(2,6-diisopropyl-4-nitrophenyl)pyridine-2,6-dicarboxamidate(2-)
OAT	oxygen atom transfer
O ^{Me₂} N4(tren)	3-((2-(bis(2-aminoethyl)amino)ethyl)imino)-2-methylbutane-2-oxide)(-)
OTf	triflate, trifluoromethanesulfonate
PCET	proton-coupled electron transfer
PCN	2-((di- <i>tert</i> -butylphosphanyl)methyl)-6-((dimethylamino)methyl)benzen-1-ide
pipN ₂ ^{<i>i</i>Pr₂}	<i>N,N'</i> -bis(2,6-diisopropylphenyl)-1-methylpiperidine-2,6-dicarboxamidate(2-)
PT-ET	proton transfer - electron transfer
PY5Me	2,6-bis-(1,1-bis(2-pyridyl)ethyl)pyridine
PY5	2,6-bis-((2-pyridyl)methoxymethane)pyridine
pyN ₂ ^{<i>i</i>Pr₂}	<i>N,N'</i> -bis(2,6-diisopropylphenyl)pyridine-2,6-dicarboxamidate(2-)
pyN ₂ ^{Me₂}	<i>N,N'</i> -bis(2,6-dimethylphenyl)pyridine-2,6-dicarboxamidate(2-)
PyPz	tetramethyl-2,3-pyridinoporphyrzine(2+)
SCE	standard calomel electrode
SHE	standard hydrogen electrode
S ^{Me₂} N4(tren)	3-((2-(bis(2-aminoethyl)amino)ethyl)imino)-2-methylbutane-2-thiolate)(-)
TBP8Cz	octakis(<i>p-tert</i> -butylphenyl)corrolazinato(3-)
^{<i>t</i>Bu} salophen	6,6'-((1,2-phenylenebis(azanylyl-idene)))bis(methanylylidene))bis(2,4-di-

	<i>tert</i> -butylphenolate)(2–)
TEMPOH	2,2,6,6-tetramethyl-piperidin-1-ol
TEMPO	(2,2,6,6-tetramethyl-piperidin-1-yl)oxyl
<i>terpy</i>	2,2';6',2'-terpyridine
THF	tetrahydrofuran
13-TMC	1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclotridecane
TMC	tetramethylcyclam, 1,4,8,11-tetramethyl 1,4,8,11 tetraazacyclotetradecane
TMG ₃ tren	tris(2-(<i>N</i> 2-tetramethylguanidyl)ethyl)amine
TOF	time of flight
Tpf	tris(pentafluorophenyl)corrolate(3–)
UV-Vis	ultraviolet - visible
XANES	X-ray absorption near-edge spectrum
XAS	X-ray absorption spectroscopy
XRD	X-ray diffraction

Contents

Summary	i
Acknowledgements	iii
Abbreviations	v
1 Introduction	1
1.1 The oxidation of hydrocarbons	2
1.1.1 Oxidations in biology	2
1.2 Reactive metal-oxygen species	3
1.2.1 Hydrogen atom transfer	4
1.2.2 Other modes of reactivity	7
1.3 Early and late transition metals	7
1.3.1 Molecular orbital structure	8
1.3.2 Model oxo-complexes of the late transition metals	9
1.4 M–O–X oxidants	10
1.4.1 Model complexes of lipoxygenase	11
1.4.2 Comparison of Mn/Fe=O and –OH complexes	14
1.4.3 Lewis acid metal-oxygen adducts	19
1.4.4 Late transition M–O–X complexes	23
1.4.5 Comparative reactivity trends	25
1.5 Nickel-based oxidations	31
1.5.1 Enzymes and synthetic catalysts	31
1.5.2 Model complexes	32
1.6 Aims & methods	32
References	35
2 Characterisation and Oxidising Reactivity of a Nickel(III) Bicarbonate Complex	41
2.1 Introduction	42
2.2 Formation and characterisation of a nickel(III) bicarbonate complex	42
2.2.1 EPR spectroscopy	44

2.2.2	X-Ray absorption spectroscopy	46
2.2.3	DFT calculations	48
2.3	Oxidative reactivity	49
2.3.1	Oxidation of O–H bonds	49
2.3.2	Oxidation of other substrates	50
2.4	Conclusions	51
2.5	Experimental section	52
	References	58
3	Tuning of the Reactivity of Nickel(III)–Oxygen Adducts in O–H and C–H	
	Bond Activation	61
3.1	Introduction	62
3.2	Synthesis and characterisation of nickel(II) complexes	62
3.3	Formation and characterisation of nickel(III) complexes	63
3.3.1	EPR spectroscopy	66
3.3.2	Mass spectroscopy	66
3.3.3	X-Ray absorption spectroscopy	68
3.3.4	DFT calculations	70
3.4	Oxidative reactivity	73
3.4.1	Oxidation of O–H bonds	73
3.4.2	Oxidation of C–H bonds	78
3.5	Conclusions	81
3.6	Experimental section	82
	References	93
4	Modulation of the Coordination Environment of Nickel(II) and (III) Pyridi-	
	nedicarboxamidate Complexes	95
4.1	Introduction	96
4.2	Synthesis and characterisation of nickel(II) complexes	96
4.2.1	Synthesis	96
4.2.2	Crystal structures	99
4.2.3	Spectroscopy and magnetic properties	101
4.2.4	Electrochemical properties	104
4.3	Formation and characterisation of nickel(III) complexes	106
4.3.1	EPR spectroscopy	108
4.3.2	Preliminary reactivity studies	111
4.4	Conclusions	113

4.5	Experimental section	115
	References	127
5	Evidence for a Transient High Valent Oxidant in the Reaction of a Nickel(II) Complex with <i>m</i>-CPBA	129
5.1	Introduction	130
5.2	Synthesis of a nickel(II) acetonitrile complex and reaction with <i>m</i> -CPBA .	130
5.3	Synthesis and oxidation of a nickel(II) 3-chlorobenzoate complex	132
5.4	Analysis of decay products	134
5.4.1	Formation of a benzoxazine-containing modified ligand	135
5.4.2	Secondary ligand degradation products	140
5.5	Oxidation of exogenous substrates	140
5.6	Conclusions	141
5.7	Experimental section	142
	References	151
6	Synthesis of Cobalt(II) and Zinc(II) Pyridinedicarboxamidate Complexes .	153
6.1	Introduction	154
6.2	Synthesis and characterisation of a cobalt(II) acetonitrile complex	155
6.3	Formation of cobalt(II) acetate complexes	157
6.4	Synthesis and characterisation of zinc(II) complexes	161
6.5	Electrochemical investigation of the zinc(II) acetate complex	163
6.6	Conclusions	164
6.7	Experimental section	167
	References	173
7	Conclusions and Future Work	175
7.1	Summary and conclusions	176
7.2	Future work	179
Appendix A		181
A.1	Chapter 2	181
A.2	Chapter 3	186
A.3	Chapter 4	209
A.4	Chapter 5	228
A.5	Chapter 6	236

Chapter 1

Introduction

1.1 The oxidation of hydrocarbons

Oxidation reactions constitute a large and varied class of transformations which are employed in syntheses ranging from laboratory scale to fine chemicals and large-scale commodities.¹ Various directions of research in the field are aimed at improving the selectivity and yields of products, employing milder conditions and inexpensive and non-polluting reagents: catalytic methods, utilising atmospheric dioxygen or hydrogen peroxide, would be in this sense particularly attractive.

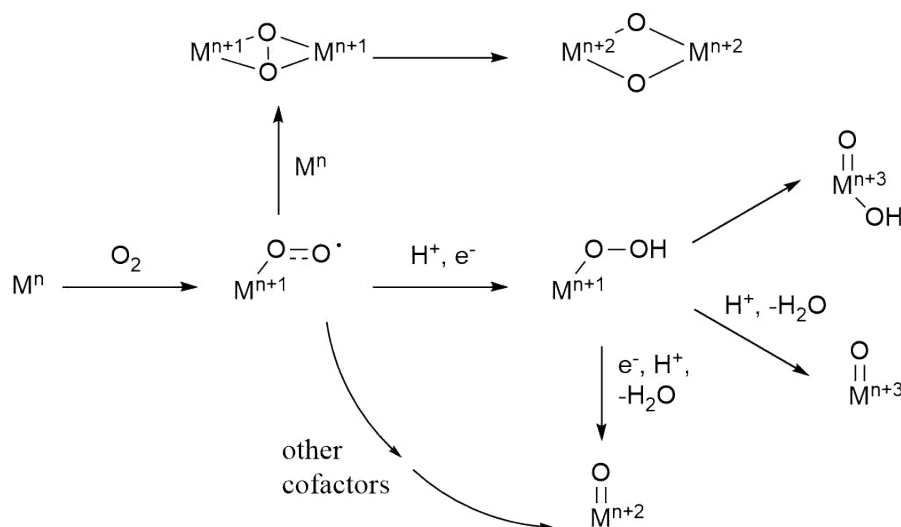
A class of substrates of great interest is represented by hydrocarbons. Alkanes make up an abundant source of organic feedstock for the chemical industry. Several factors however hamper their transformation into higher-value products. Specifically, their C–H bonds are quite inert and require harsh conditions to react, leading to energy-intensive and poorly selective processes. For example, cracking and dehydrogenation are endothermic reactions which require high temperature and pressures. On the contrary, oxidative functionalisations, using atmospheric oxygen, are exothermic processes which could potentially couple energy production and transformations such as the conversion of alkanes into the corresponding alcohols, aldehydes and carboxylic acids.² Unfortunately for these reactions selectivity is a major issue. In general, the functionalised products are more reactive than the starting materials, leading to overoxidation if a large excess of substrate is not used.

In summary, the twofold challenge of activating both dioxygen and inert substrates under mild conditions represents a major hurdle to the oxidative functionalisation of hydrocarbons. These issues could potentially be overcome by the development of new oxidation catalysts, offering notable rewards from both the economic and the environmental points of view.

1.1.1 Oxidations in biology

One of the most promising approaches to the design of catalysts capable of the selective oxidation of inert substrates is the emulation of biological systems.³ Numerous oxidation reactions, including the hydroxylation of inert C–H bonds, are catalysed by metalloenzymes. These enzymes operate under physiological conditions of temperature and pressure: if this chemistry could be replicated in an industrial process, the energy demand would be greatly reduced compared to the present state of the art. The metals at the core of the enzymes' active sites (primarily iron and copper), are abundant in the earth's crust and of limited toxicity, lending themselves to large-scale use.

While a variety of mechanisms and reactive species has been hypothesised for the oxidation reactions catalysed by metalloenzymes, they possess certain common features.^{3,4} In the first place, the dioxygen molecule binds to the metal, concomitantly with its one-electron reduction, to form a superoxide (O_2^-) ligand. Further activation of the O_2 fragment is induced through its progressive reduction, with population of its antibonding orbitals leading to a lowered O–O bond order. The necessary reducing equivalents can be provided by a second metal centre or by external cofactors, including NAD(P)H, flavin, ascorbate,⁵ tetrahydropterin, α -ketoacids, or several electron-transfer proteins (sch. 1.1).⁶ In some cases no sacrificial reductant is needed, as the substrate undergoes a 4-electron oxidation.^{7,8}



Scheme 1.1. Dioxygen activation and generation of high-valent intermediates in enzymatic oxidations.

Superoxo, peroxo and hydroperoxo intermediates have been shown to be able to directly attack substrates in specific cases;⁴ nevertheless, the actual oxidant that performs substrate activation is more commonly formed after scission of the O–O bond. These oxidants include terminal, high-valent metal-oxygen adducts which can be described as possessing oxo or oxyl ligands, depending on their electronic structure (*e.g.* $\text{Fe}^{\text{IV}}=\text{O}$, $\text{Fe}^{\text{V}}(\text{OH})=\text{O}$, $(\text{L}^{\bullet+})\text{Fe}^{\text{IV}}=\text{O} \longleftrightarrow (\text{L})\text{Fe}^{\text{V}}=\text{O}$, $\text{Cu}^{\text{II}}-\text{O}^{\bullet} \longleftrightarrow \text{Cu}^{\text{III}}=\text{O}$), and dinuclear bridging-oxo species (*e.g.* $\text{Fe}^{\text{IV}}_2(\mu\text{-O})_2$, $\text{Cu}^{\text{III}}_2(\mu\text{-O})_2$).

1.2 Reactive metal-oxygen species

Because of issues associated with applying enzymatic processes on the industrial scale, the synthesis of small-molecule, bioinspired complexes acquires great importance. Further-

more, biomimetic complexes can be useful in elucidating both enzymatic and biomimetic mechanisms, through the study of their reactivity, and the structural and spectroscopic examination of intermediates. In turn, this understanding can point the way towards more effective catalysts.

Mononuclear metal oxos are the most widely studied reactive intermediates: the observation of high-valent iron oxo species, both in synthetic and enzymatic haem systems, dates back to the 1980s.^{9–11} By contrast, a non-haem $\text{Fe}^{\text{IV}}=\text{O}$ complex, $[\text{Fe}(\text{O})(\text{TMC})(\text{MeCN})]^{2+}$ (TMC = tetramethylcyclam), was only isolated and crystallographically characterised in 2003,¹² spurring a great interest in the field. Numerous oxo complexes of iron (as well as manganese and chromium) in high oxidation states have been synthesised, and shown to be competent oxidants in diverse reactions, including the hydroxylation of inert alkanes such as cyclohexane.^{13–15} This has led to a good understanding of these compounds, although they show a remarkable complexity in their reactivity and how it is modulated by ligand effects, the presence of Lewis acids, and other conditions.

Terminal oxidants based on the later transition metals (Co, Ni and Cu) represent a new research directions that has begun to garner attention in recent years. They are expected to display novel and more potent reactivity, together with a higher instability (section 1.3). Finally, in many synthetic systems, the diverse range of supporting ligand environments, and the use of oxidants other than O_2 , can lead the isolation of a great structural variety of oxidising intermediates, aside from metal oxos. These are generally less well known, but nevertheless display interesting properties and reactivity (section 1.4).

1.2.1 Hydrogen atom transfer

A variety of oxidation reactions are performed by biological and synthetic metal-oxygen oxidants (fig. 1.1),^{16–18} corresponding to a range of different mechanisms. A critical elementary step is that of hydrogen atom transfer (HAT, also called hydrogen atom abstraction, HAA), which is involved in the activation of C–H bonds and in their oxidations (*i.e.* aliphatic hydroxylation, oxidative dehydrogenation, N/O-dealkylation). Hydrogen atom transfer and affine mechanisms have been extensively studied in different fields (*e.g.* combustion, atmospheric chemistry), resulting in a lack of universally agreed descriptions and definitions. For the purpose of consistency, the nomenclature scheme proposed by Mayer will be referred to throughout this thesis.¹⁹

The general class of reactions in which a proton and an electron are transferred from a donor to an acceptor molecule is called proton-coupled electron transfer (PCET). Depending on whether the two particles are transferred in a single kinetic step (*i.e.* without the

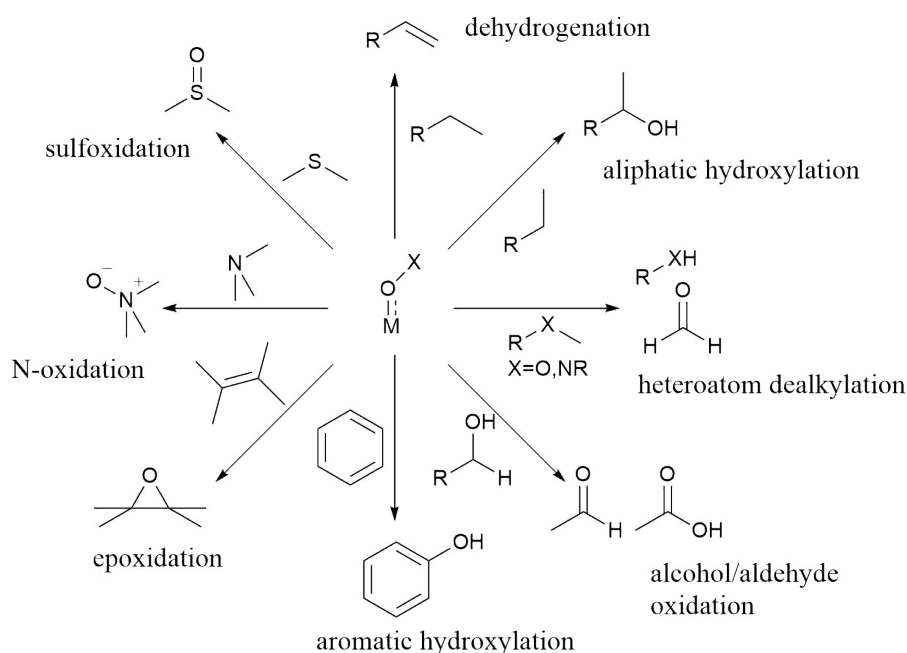


Figure 1.1. Oxidation reactions mediated by biological metal-oxygen intermediates.

formation of intermediates), or in two, one can further classify concerted proton-electron transfer (CPET), proton transfer - electron transfer (PT-ET, when the proton is transferred first) and electron transfer - proton transfer (ETPT, in which the electron is transferred first). Furthermore, even within the concerted reaction, the transfer of the two particles can be synchronous (*i.e.* they are transferred to the same degree in the transition state) or not; and they can be transferred to the same atom, or to different locations in the acceptor molecule. I will talk of HAT/HAA for any CPET reaction with synchronous H^+ and e^- transfer to the same acceptor molecule, irrespectively of their destinations within it.

Extensive studies on CPET reactions have led to the development of structure-reactivity relationship models. A simple observation is that the rate of the reaction is correlated with its thermodynamic driving force.²⁰ The existence of a linear relationship between the reaction enthalpy and the activation energy ($E_a = E_0 + \alpha\Delta H^\circ$), within a family of simple reactions, was recognized from early kinetic and theoretical studies (Bell-Evans-Polanyi principle).^{21,22} In a HAA reaction the ΔH° is equal to the difference between the bond dissociation energies (BDE) of the E-H bond that is broken in the substrate (C-H in a hydrocarbon) and the E-H bond that is formed in the oxidant (O-H in the case of a metal-oxygen adduct). An important consequence of the linear free energy relationship is that a higher-energy intermediate will display higher reaction rates, as well as provide the driving force for the activation of stronger C-H bonds.

In rigorous terms, the theoretical derivation of the relationship is valid for free energies rather than enthalpies, and ΔG° and bond dissociation free energies (BDFE) should be used. Nevertheless, BDEs are often used in the literature instead, because of the somewhat lower availability of experimental BDFE data; this constitutes a reasonable approximation in the absence of large entropic effects.

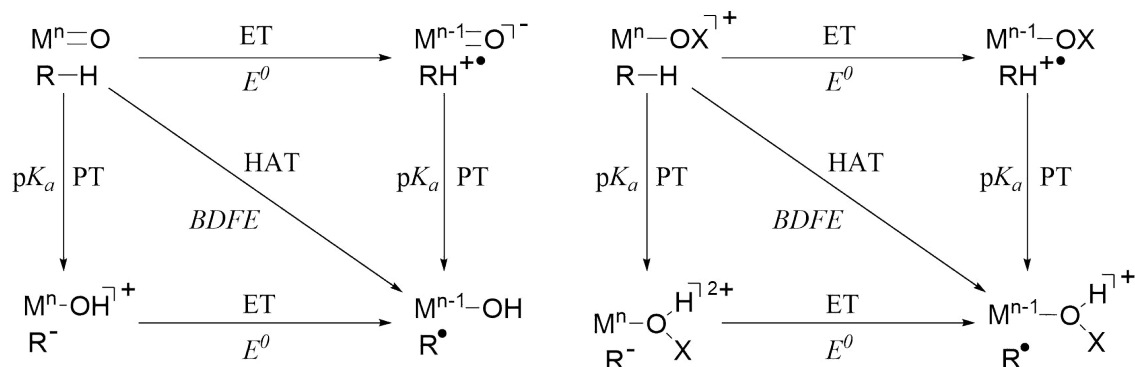


Figure 1.2. Relationships between HAT, ET, PT and the intermediates involved, for a $M=O$ oxidant (left) and for a generic $M-O-X$ oxidant (right).

The $BDFE_{O-H}$ is thus the crucial thermodynamic parameter determining the oxidising power of an hydrogen atom abstractor. As a free energy, it can be decomposed into the sum of those of the two steps of proton and electron transfer (fig. 1.2), which can be more easily measured as equilibrium acidities (pK_a) and redox potentials (E°). This is very useful for the determination of solution BDFEs through the use of a thermochemical cycle; this approach was pioneered by Bordwell,²³ using the following equation, in which the constant C_{sol} is related to the free energy of the $H^\bullet/H^+$ reduction in the given solvent.

$$BDFE_{sol}(X-H) = 1.37pK_a + 23.06E^\circ + C_{sol}$$

It is evident that the reduction potential of a compound alone is not an accurate indicator of its oxidising power. Moreover, the parameters are correlated, in that a given structural modification will generally have opposite effects on the BDE_{O-H} ; an increase in electron-richness will correspond to an increased basicity but a lower reduction potential, and *vice versa*.

In the last decades several theoretical approaches have been developed to describe the HAT reactivity for metal complexes.^{24–27} Mayer has applied a Marcus-theory based approach from which he rederived the aforementioned linear-free energy relationship.^{20,28–30} In addition to that, Marcus theory provided some other predictions; specifically, the $\Delta^\ddagger G/\Delta G^\circ$

slope should be close to -0.5 for reactions that are not too exo- or endoergonic. Moreover, an additional parameter explains the experimental observations of stark differences in HAT rates for certain reactions which have similar driving forces. For example, O–H bonds (in phenols or hydroxylamines) consistently react much faster than C–H bonds with the same $\text{BDFE}_{\text{X-H}}$. The intrinsic difference in reactivity is attributed to the self-exchange rates: the rate of the reaction $\text{RO}^\bullet + \text{ROH} \rightarrow \text{ROH} + \text{RO}^\bullet$ is higher than that of $\text{R}_3\text{C}^\bullet + \text{R}_3\text{CH} \rightarrow \text{R}_3\text{CH} + \text{R}_3\text{C}^\bullet$, in spite of both having $\Delta G^\circ = 0$.

1.2.2 Other modes of reactivity

Aside from the HAT/PCET reactions described above, several other elementary mechanisms can be at play in the oxidation of organic substrates. Aromatic C–H bonds have very large homolytic bond dissociation energies (*e.g.* benzene has $\text{BDE}_{\text{C-H}} = 113 \text{ kcal/mol}^{31}$), making their activation via HAT quite thermodynamically unfavourable. In fact, the aromatic hydroxylation by terminal and bridging oxo complexes has been shown to proceed through an electrophilic aromatic substitution mechanism.^{32–34}

Another class of reactions, including alkene epoxidation and the oxidation of heteroatoms (phosphine to phosphine oxide, sulfide to sulfoxide and sulfone, amine to N-oxide), corresponds to the net transfer of an O atom to an electron rich substrate. This can happen in a single, concerted step (oxygen atom transfer, OAT), but can also be initiated by a single electron transfer, to form a radical cation (*i.e.* $\text{Ph}_3\text{PO}^{+\bullet}$), which then reacts further to give the oxygenated product. In general, simple electron transfer, as opposed to concerted group transfer processes (HAT, OAT), are favoured for oxidants with a large reduction potential.

Oxidants can also display nucleophilic behaviour, typically attacking an electron-poor carbon atom such as in the carbonyl group of carboxylates and aldehydes. This has been observed or hypothesised predominantly for peroxo, superoxo and μ -oxo species both in enzymes^{35,36} and model complexes.^{4,37,38}

1.3 Early and late transition metals

As noted above (section 1.2), a large number of the highly oxidising metal-oxygen intermediates come from groups 6–8 of the periodic table. This is especially true for terminal metal-oxo complexes. In fact, a trend in transition metal chemistry is quite evident, in that the early transition metals give highly stable, inert oxocomplexes (*e.g.* $\text{V}^{\text{IV}}\text{O}^{2+}$, $\text{Ti}^{\text{IV}}\text{O}^{2+}$),

whereas on moving to the right in the period the complexes become less stable and more reactive.³⁹ One can then foresee that metals to the right of the *d*-block, possessing higher electronegativities and less stable high oxidation states, would produce stronger oxidising agents.

Their isolation has proved a difficult experimental challenge, but computational studies have been carried out which support this hypothesis. Pierpont and Cundari investigated a series of Fe, Co, and Ni oxo complexes supported by bidentate ligands, and predicted them to be capable of hydroxylating methane.⁴⁰ The later metals were found to be more reactive, with activation barriers as low as 8.1 kcal/mol in the case of a Ni^{III}=O with a fluorinated β -diketiminato ligand. Similarly, both [Cu^{III}(O)(L)] and [Cu^{III}(OH)(L)]⁺ complexes were predicted by Cramer and coworkers to carry out the same reaction with $\Delta^\ddagger H$ of 14.7 and 23.0 kcal/mol respectively.⁴¹ Computations as well showed bare M^{III}O⁺ ions to be capable of oxidising methane, with later transition metals being more effective.⁴² The hydroxylation of alkanes by Cu^{III}O was also demonstrated experimentally by the reaction of [Cu^{III}(O)(phenanthroline)]⁺ with propane in an ion beam.⁴³ The CoO⁺ ion has also been shown to activate small alkanes (C₁–C₅) in the gas phase.⁴⁴

1.3.1 Molecular orbital structure

The ligand field model developed by Ballhausen and Gray in 1963 to describe the electronic structure of metal oxo complexes in tetragonal symmetry,^{45,46} is also explanatory of the destabilisation incurred with the increasing *d*-electron count of the metal. The interaction of the O²⁻ ligand with the metal centre gives rise to three bonding orbitals, which are mostly of *s/p*_O character and occupied, and three corresponding antibonding orbitals, which have mostly *d*-character (fig. 1.3, left). For a *d*⁰ ion, then, one has a M=O bond order of 3, conferring remarkable stability. In a tetragonal field, any *d* electron after the first two has to occupy antibonding orbitals, destabilising the oxo ligand and increasing M ^{δ +}–O ^{δ -} polarisation and the oxygen basicity. Taking into account realistically achievable oxidation states, Fe^{IV}=O, *d*⁴, is the rightmost possible multiply bond metal-oxygen adduct, and an “oxo wall” separates groups 8 and 9 (although *d*⁴ Ir^V=O has been reported⁴⁷).

This model is only strictly valid for a tetragonal coordination environment. One could envision that 3- or 4- coordination of the metal, in contrast to the octahedral, square pyramidal and trigonal bipyramidal geometries common in Fe=O chemistry, can relieve some of the M–O antibonding interactions. Lowering the coordination number frees up some of the *d*-like orbitals as non-bonding orbitals, reducing the strain caused by high *d*-electron

counts. The diagram for the square-planar case is shown in the right side of fig. 1.3. Compared to the tetragonal case, the two lowest-energy d -block orbitals are nonbonding with respect to the M–O interaction; so that a bond order of 2 can be maintained for a d^6 configuration, as opposed to d^4 in a low-spin octahedral complex.

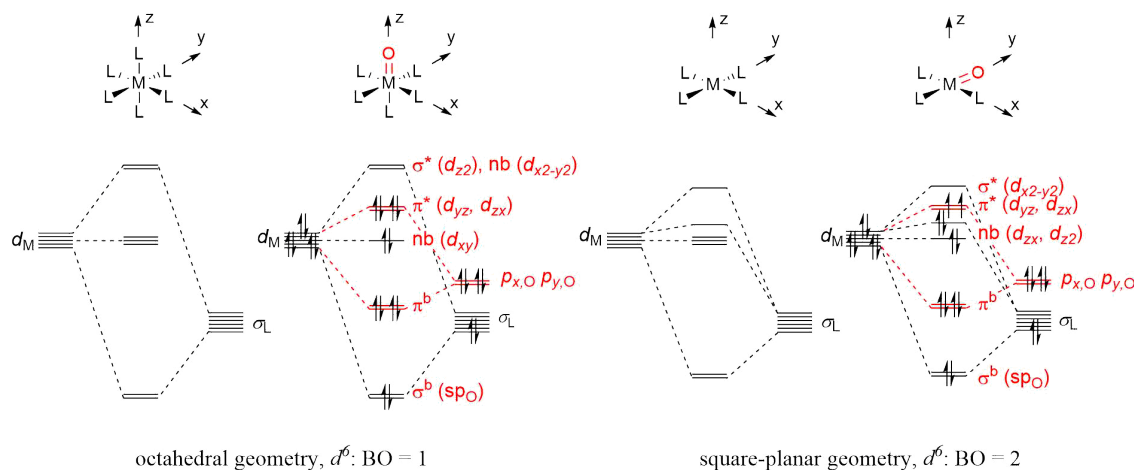


Figure 1.3. Schematic orbital energy diagram for M=O bonding in octahedral (left) and square planar (right) geometries. Only interactions involving the d -block are included for simplicity. Molecular orbitals are labelled according to the local symmetry and bonding character relative to the M–O bond, and the prevalent atomic orbital contribution.

1.3.2 Model oxo-complexes of the late transition metals

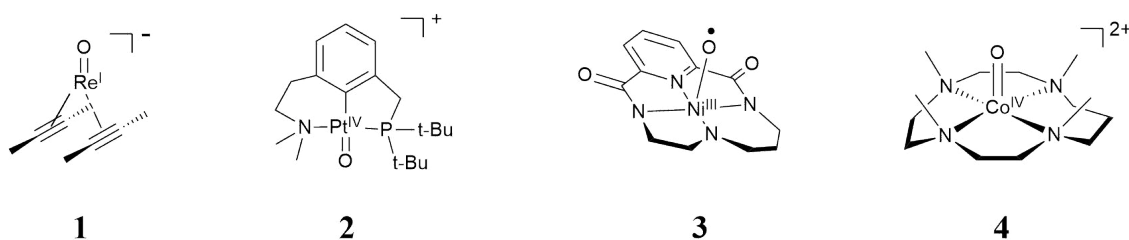


Figure 1.4. Selected examples of metal oxos with $d > 4$.

Only a few transition metal terminal oxo complexes with five or more d valence electrons have been reported in the literature (fig. 1.4). Cundari reported a series of rhenium(I) (d^6) complexes, $[\text{Re}^{\text{I}}(\text{O})(\text{alkyne})_2]^-$ (**1**).⁴⁸ A peculiarity of these complexes is the presence of the strongly π -accepting alkyne ligands; computation of their electronic structures demonstrated the delocalisation of the frontier molecular orbitals over them, as well as the effect of low coordination number in allowing an oxo- and alkyne-based non-bonding orbital.

Amongst the late transition metals, Milstein obtained a $[\text{Pt}^{\text{IV}}(\text{O})(\text{PCN})]^+$ (**2**, $\text{PCN} = \text{C}_6\text{H}_3[\text{CH}_2\text{P}(\text{tBu})_2](\text{CH}_2)_2\text{N}(\text{CH}_3)_2$), by oxygen atom transfer from dimethyldioxirane to a square-planar Pt^{II} precursor.⁴⁹ Other than an unusual water activation reaction, yielding a Pt^{IV} dihydroxo complex, **2** had unremarkable reactivity. A contributing factor may be the higher metal-ligand bond strength and stability of the high oxidation states for third-row metals, compared to the first row.

Recently, Company reported a metastable, high-valent nickel complex supported by a bis-amidato macrocyclic ligand.⁵⁰ $[\text{Ni}^{\text{III}}(\text{O}^\bullet)(\text{L})]$ (**3**) was obtained from the reaction of the $[\text{Ni}^{\text{II}}(\text{L})]$ precursor with *m*-chloroperbenzoic acid (*m*-CPBA). While **3** could be seen as a formal nickel(IV)-oxo compound, according to computational and spectral evidence it is more appropriately described as a nickel(III)-oxyl compound, with a Ni-O single bond order. **3** showed a remarkable reactivity, affecting the sulfoxidation of thioanisole derivatives, the epoxidation of alkenes and HAA from hydrocarbons including cyclohexane (BDE = 99 kcal/mol).

Finally, Ray and coworkers have investigated a cobalt(IV)-oxo complex.⁵¹ $[\text{Co}^{\text{II}}(13\text{-TMC})(\text{OTf})]^+$ (13-TMC = 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclotridecane) was converted into $[\text{Co}^{\text{IV}}(\text{O})(13\text{-TMC})]^{2+}$ **4** by chemical oxidation with PhIO, or under photochemical conditions with $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$, $\text{Na}_2\text{S}_2\text{O}_8$ and water. **4** was capable of HAT from hydrocarbons (including fluorene, BDE = 80 kcal/mol), and of OAT to alkenes and $[\text{Fe}^{\text{II}}(\text{TMC})]^{2+}$, forming $[\text{Fe}^{\text{IV}}(\text{O})(\text{TMC})]^{2+}$. Interestingly, DFT calculations indicated an unusual electronic structure, in which, in spite of a tetragonal ligand field, a relatively low-energy $d_{x^2-y^2}$ is non-bonding with respect to the Co-O bonding (but anti-bonding with respect to the plane's Co-N bonds).

1.4 M–O–X oxidants

Aside from $\text{M}=\text{O}$ complexes, various other $\text{M}-\text{O}-\text{X}$ entities are capable hydrocarbon oxidants, and have been identified in biological systems. Lipoxygenases are a family of non-haem iron enzymes, which catalyse the oxidation of polyunsaturated fatty acids.^{52,53} In their catalytic cycles, an $\text{Fe}^{\text{III}}-\text{OH}$ is responsible for HAT from a weak C–H bond in the substrate.^{52–56} There is also evidence for an analogous $\text{Mn}^{\text{III}}-\text{OH}$ oxidant in an Mn-lipoxygenase.^{57–59} Galactose oxidase is another enzyme which exploits an aryloxo-metal oxidant: it performs the two-electron oxidation of alcohols to aldehydes through a combination of a Cu^{III} couple and a metal bound tyrosyl radical.^{60,61} The presence of these $\text{M}-\text{O}-\text{X}$ intermediates in enzymatic cycles has prompted the study of related model complexes.

1.4.1 Model complexes of lipoxygenase

There is a substantial body of hydroxo and alkoxo complexes of Mn^{III} , Fe^{III} , and Ru^{III} which are capable of HAT reactivity, making them excellent models to study the chemistry of the lipoxygenases. The first attempts at preparing models of this active site focussed on replicating the coordination environment, *i.e.* synthesising mononuclear complexes with $\text{Fe}^{\text{III}}\text{-OH}$ or $\text{Fe}^{\text{III}}\text{-OCH}_3$ cores, but these generally were not proficient at HAT from hydrocarbons.^{62–64}

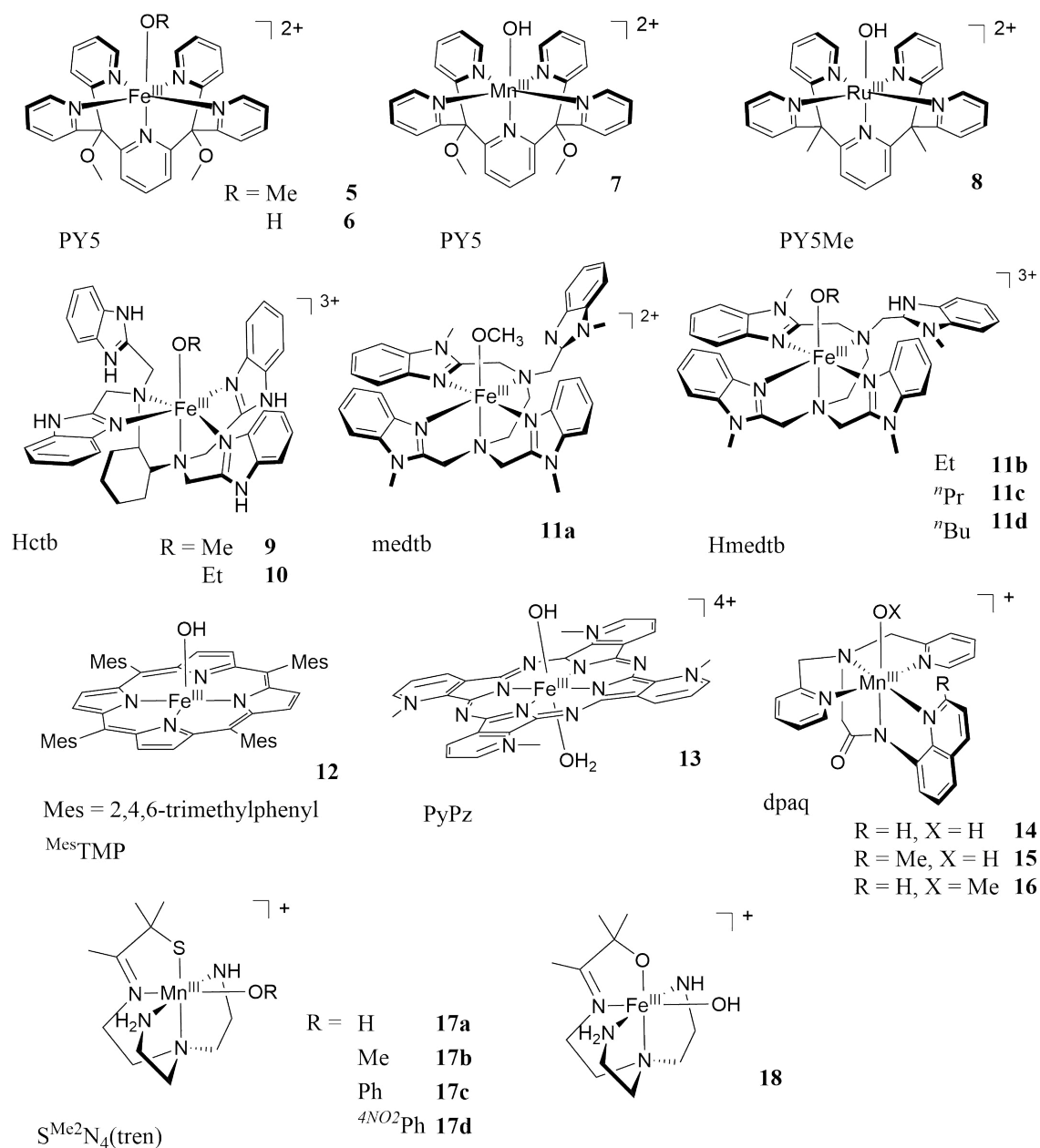


Figure 1.5. Examples of hydroxo and alkoxo Mn^{III} , Fe^{III} , and Ru^{III} complexes.

Neutral pyridine and imidazole ligands

The first breakthrough was the synthesis of $[\text{Fe}^{\text{III}}(\text{OCH}_3)(\text{PY5})](\text{OTf})_2$ (**5**, fig. 1.5), a stable ferric complex.^{65,66} **5** was shown to react with a series of hydrocarbons: a linear correlation between reaction rates and $\text{BDE}_{\text{C-H}}$ in the substrates, as well as a $\text{KIE} = 5.5$, implied a HAT mechanism. Remarkably the $\text{BDE}_{\text{C-H}}$ of some of the oxidised C–H bonds (the highest was toluene, 89 kcal/mol) was notably higher than the $\text{BDE}_{\text{O-H}}$ of the newly formed $\text{Fe}^{\text{II}}\text{--O}(\text{CH}_3)\text{--H}$ (measured as 83.5 kcal/mol), *i.e.* the reaction enthalpy was decidedly positive. A crucial feature was the $\text{Fe}^{\text{III/II}}$ reduction potential of 0.660 V (vs SHE), which is especially high and similar to that of soybean lipoxygenase (0.6 V vs SHE).⁶⁷ Such a potential is likely necessary to enhance the oxidising capability of the ferric oxidation state.

Subsequent work on the complexes $[\text{Fe}^{\text{III}}(\text{OH})(\text{PY5})]^{2+}$ (**6**, fig. 1.5) and $[\text{Mn}^{\text{III}}(\text{OH})(\text{PY5})]^{2+}$ (**7**, fig. 1.5) showed effects of ligand and metal on the HAT reactivity.^{68,69} The hydroxo Fe^{III} complex **6**, which corresponds more closely the $\text{Fe}^{\text{III}}\text{--OH}$ intermediate in lipoxygenase, showed diminished oxidising capabilities from the thermodynamic point of view when compared to the methoxide **5**: both the reduction potential (**6**: 0.56; **5**: 0.66 V) as well as the $\text{BDE}_{\text{O-H}}$ for the protonated, Fe^{II} forms resulting from HAT (**6H**: 80; **5H**: 83.5 kcal/mol) were lower. Curiously, it was a kinetically better oxidant ($k_2(\text{6} + \text{DHA})/k_2(\text{5} + \text{DHA}) = 3.6$); this effect has been suggested to be due to the increased steric hindrance of the --OCH_3 group as opposed to the --OH group. Conversely, substitution of Fe^{III} with Mn^{III} made for a better oxidant, both from the thermodynamic ($\text{BDE}_{\text{O-H}}$ of **7H** = 82 kcal/mol) and kinetic ($k_2(\text{7} + \text{DHA})/k_2(\text{6} + \text{DHA}) = 3.7$) points of view. It was noted that the transition from Mn^{III} to Mn^{II} entailed a large structural reorganisation, because of Jahn-Teller effects that are present in the Mn^{III} compound but not in Mn^{II} (or $\text{Fe}^{\text{III/II}}$). This did not hamper the reaction kinetics, in comparison to **6**, although it may contribute to a relative insensitivity of the reaction rates to the substrate $\text{BDE}_{\text{C-H}}$.

A similar Ru^{III} complex, $[\text{Ru}^{\text{III}}(\text{OH})(\text{PY5Me})]^{2+}$ (**8**, fig. 1.5), has also been reported, although its oxidative reactivity was only tested against hydroquinone substrates and ascorbic acid.⁷⁰ HAT was shown to be the mechanism for the more electron-poor substrates. Fluoro- and chlorohydroquinones, as well as ascorbic acid, were oxidised with $\text{KIEs} = 1.2$ - 1.7 and only a weak dependence of reaction rate on their oxidation potential. More electron rich hydroquinones, on the other hand, reacted by initial electron transfer followed by deprotonation, and reaction rates were strongly affected by their E_0 .

Ligands with benzoimidazole donors have also been explored: $[\text{Fe}^{\text{III}}(\text{OCH}_3)(\text{Hctb})]^{3+}$ (**9**, fig. 1.5) and $[\text{Fe}^{\text{III}}(\text{OEt})(\text{Hctb})]^{3+}$ (**10**, fig. 1.5)⁷¹ were shown to oxidise DHA with $\text{KIE} =$

5.1. Importantly, they also exhibited lipoxygenase-like activity, catalysing the oxidation of linoleic acid in the presence of dioxygen. Their high +3 charge state, due to the protonated state of a non-ligated imidazole moiety, led to high, irreversible $E_{ox} = 0.9$ V vs SHE in CH_3OH ; nevertheless their reaction rate with DHA is one fifth of that of **6** under the same conditions.

The series of complexes $[\text{Fe}^{\text{III}}(\text{OCH}_3)(\text{medtb})]^{2+}$ (**11a**, fig. 1.5) and $[\text{Fe}^{\text{III}}(\text{OR})(\text{Hmedtb})]^{3+}$ (**11b-d**, R = Et, ⁿPr, ⁿBu, fig. 1.5) also oxidised DHA with reaction rates in the same order of magnitude, and KIEs = 1.9 (**11a**) and 3.2 (**11b**).⁷² A redox potential $E_0 = 0.79$ V vs SHE was measured for the $\text{Fe}^{\text{III/II}}$ couple in **11a** (for **11b-d** the measurements were complicated by binding competition between alkoxide and solvent molecules). In spite of a correlation between the alcohol chain length and the $\text{Fe}^{\text{III}}\text{--O}$ bond distances, implying a gradation of electron donation, no corresponding effect was found on reaction rates in DHA oxidation.

Anionic ligands

A hydroxo Fe^{III} complex, supported by the ^{Mes}TMP ligand, $([\text{Fe}^{\text{III}}(\text{OH})(^{\text{Mes}}\text{TMP})])$, **12**, fig. 1.5) was capable of catalysing the disproportionation of TEMPOH. TEMPOH possesses a remarkably weak O–H bond ($\text{BDE}_{\text{O–H}} = 70.6$ kcal/mol in CH_3CN), and the catalytic step in which it is oxidised was shown to occur through HAT.⁷³ In contrast, the cationic porphyrinoid ligand PyPz has recently been shown to form a highly reactive $\text{Fe}^{\text{III}}\text{--OH}$, $([(\text{PyPz})\text{Fe}^{\text{III}}(\text{OH})(\text{OH}_2)]^{4+}$, **13**, fig. 1.5).⁷⁴ It was found to oxidise stronger C–H bonds (diphenylmethane, 82 kcal/mol) and its reaction rate with DHA was very high ($73 \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C, KIE = 21). This result is suggestive of the importance of high oxidation potentials of the $\text{M}^{\text{III}}\text{--OH}$ oxidants, as hinted at by the early lipoxygenase models.

$\text{Mn}^{\text{III}}\text{--OH}$ complexes have also been reported, supported by anionic, amidate ligands (dpaq^{H} in **14** and its methylated analogue $\text{dpaq}^{2\text{Me}}$ in **15**, fig. 1.5).⁷⁵ The hydroxide ligand derived from dioxygen, via its activation by a Mn^{II} precursor. TEMPOH (with KIE = 1.8), xanthene, and phenols with weak O–H bonds were oxidised by both complexes. Interestingly, the methylated ligand induced an elongation of the $\text{Mn}\text{--N}_{\text{quinoline}}$ bond, and a corresponding higher reduction potential (-0.02 vs -0.15 vs. SHE), resulting in a 240-fold increase in reaction rate towards TEMPOH. The methoxide complex, $[\text{Mn}^{\text{III}}(\text{OCH}_3)(\text{dpaq}^{\text{H}})]^+$ (**16**, fig. 1.5) also showed oxidising reactivity towards phenols.^{76,77}

Kovacs reported a series of compounds $[\text{Mn}^{\text{III}}(\text{OR})(\text{S}^{\text{Me}_2}\text{N}_4(\text{tren}))]$ (**17a-d**, R = H, CH_3 , Ph, $4\text{-NO}_2\text{Ph}$, fig. 1.5), which were characterised by ligation from a thiolate donor and by solubility in water.⁷⁸ The --OH and --OCH_3 compounds, which displayed lower reduction potentials, were capable of oxidising TEMPOH. A BDFE was determined for $\text{Mn}^{\text{III}}\text{--OH}_2$

(74 kcal/mol). Conversely, an iron analogue $[\text{Fe}^{\text{II}}(\text{OH}_2)(\text{O}^{\text{Me}_2}\text{N4}(\text{tren}))]$ (**18**, fig. 1.5) was found to have a weaker BDFE (69 kcal/mol),⁷⁹ and consequently its reaction is spontaneous in the direction $[\text{Fe}^{\text{II}}(\text{OH}_2)(\text{O}^{\text{Me}_2}\text{N4}(\text{tren}))] + \text{TEMPO} \rightarrow [\text{Fe}^{\text{III}}(\text{OH})(\text{O}^{\text{Me}_2}\text{N4}(\text{tren}))] + \text{TEMPOH}$. In this case the change from Mn to Fe, and the switch from the thiolate to a less electron-donating alkoxide donor, contributed to the lowering of both E_0 and $\text{p}K_a$ in **18** in comparison to **17aH**, thus weakening the $\text{M}(\text{O}(\text{H})-\text{H})$ bond.

1.4.2 Comparison of Mn/Fe=O and –OH complexes

Some ligands have proven versatile enough to support both $\text{M}=\text{O}$ complexes and their protonated, $\text{M}-\text{OH}$ analogues. These systems are particularly significant in allowing the direct comparison between the two terminal ligands (O^{2-} and ^-OH) in the same coordination environment, thus allowing comparisons of relative reactivity properties.

Manganese

Fuji analysed salen complexes of manganese, corresponding to various putative intermediates in the catalytic epoxidation of alkenes.^{80,81} $[\text{Mn}^{\text{IV}}(\text{O})(^{\text{Mes}}\text{salen})]$ (**19**, fig. 1.6), $[\text{Mn}^{\text{IV}}(\text{OH})(^{\text{Mes}}\text{salen})]^+$ (**19H**⁺, fig. 1.6) and $[\text{Mn}^{\text{III}}(\text{OH}_2)(^{\text{Mes}}\text{salen}^{\bullet+})]^{2+}$ (**19H**₂²⁺, fig. 1.6), while formally having the same oxidation state, displayed striking differences in reactivity, presumably as a result of the differing protonation state of the oxygen ligand. Interestingly, in spite of protonation increasing the total charge and electropositivity, the $\text{Mn}^{\text{IV}}=\text{O}$ **19** was by far the best oxidant, the only one capable of transferring oxygen atoms to phosphines and sulfides, as well as activating weak C–H bonds; the $\text{Mn}^{\text{IV}}-\text{OH}$ **19H**⁺ was limited to oxidising phenols (via HAT from the O–H bond, with $\text{BDE}_{\text{O}-\text{H}}$ of up to 83 kcal/mol), and the $[\text{Mn}^{\text{III}}-\text{OH}_2(\text{L}^{\bullet+})]$ **19H**₂²⁺, in which protonation induced an internal electron transfer with reduction of the metal to Mn^{III} and oxidation of the supporting salen ligand, showed no such reactivity.

Extensive work has been conducted on the system $[\text{Mn}^{\text{IV}}(\text{OH})_2(\text{Me}_2\text{EBC})]^{2+}$ (**20H**₂²⁺, fig. 1.6), which has the property of being subject to sequential deprotonation to give first an $\text{Mn}(\text{O})(\text{OH})$ (**20H**⁺, fig. 1.6) and then an $\text{Mn}(\text{O})_2$ form (**20**, fig. 1.6), depending on the pH of the medium.^{82–90} All three complexes were shown to oxidise a series of hydrocarbons (xanthene to fluorene): the reaction rates were about 15 times faster for **20H**⁺ as opposed to **20H**₂²⁺, and 40 times faster for **20**.^{83,84} The oxidising power trend was thus the reverse of the total charge and electropositivity of the complex. Conversely, the $\text{BDE}_{\text{O}-\text{H}}$ of the newly formed O–H bonds seemed to be the key parameter. Values were determined for **20H**

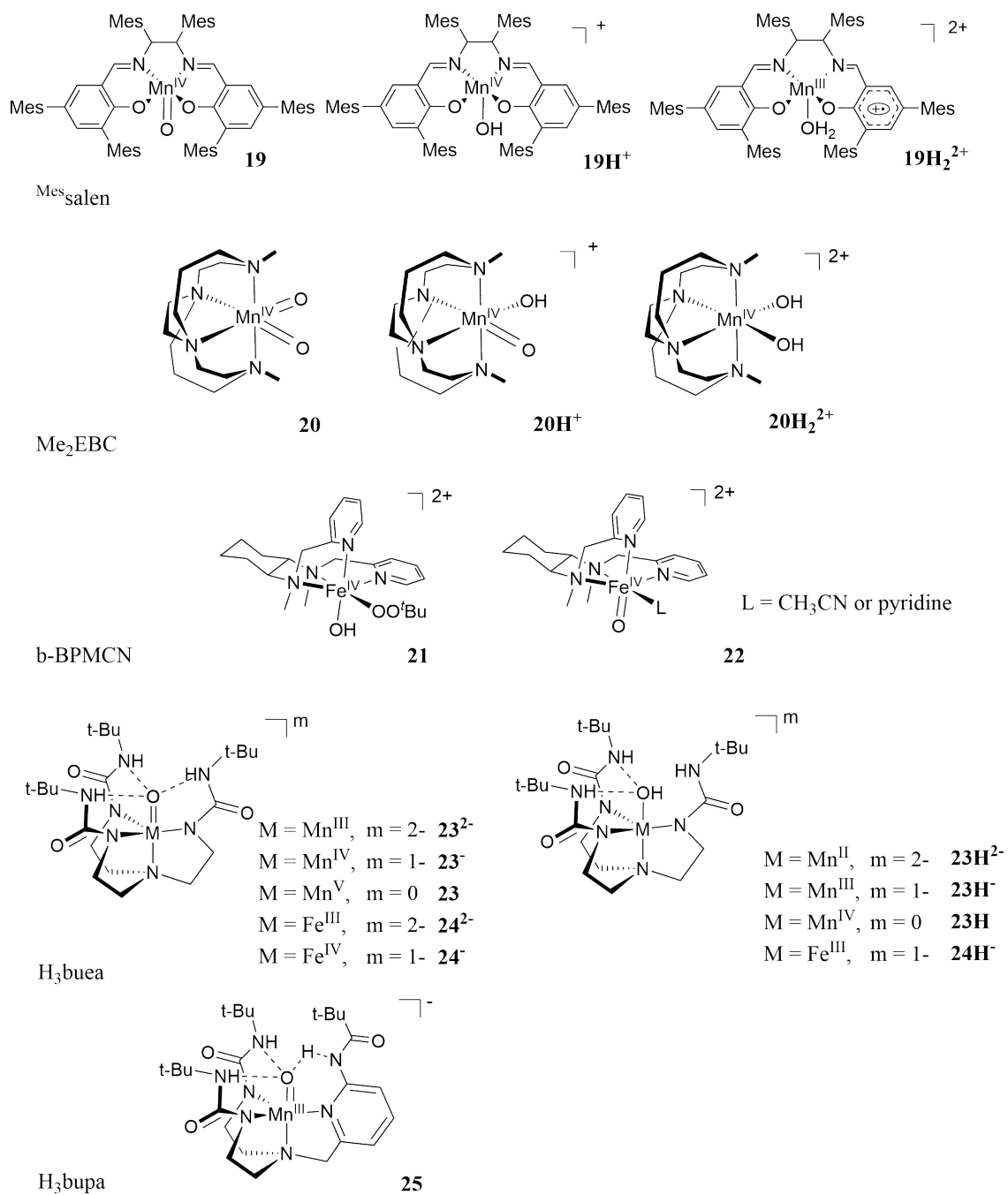


Figure 1.6. Sets of oxo, hydroxo and aquo complexes of Mn and Fe supported by the same ligand.

= $[\text{Mn}^{\text{III}}(\text{OH})(\text{OH}_2)(\text{Me}_2\text{EBC})]^{2+}$ (83.0 kcal/mol) and $20\text{H}^{2+} = [\text{Mn}^{\text{III}}(\text{OH})_2(\text{Me}_2\text{EBC})]^{2+}$ (84.3 kcal/mol). Assuming that the 1.3 kcal/mol difference is entirely reflected in the activation energies, this is sufficient to explain entirely the difference in reaction rates. KIEs of 3.3 (20H_2^{2+}) and 3.8 (**20**) were measured for the oxidation of DHA.

Computational studies showed that deprotonation of the OH moiety of 20H_2^{2+} has a large effect on the energy and composition of the π^* (Mn–O) frontier orbitals, but only minor ones on the σ^* (Mn–O). Hence it was suggested, also on the basis of steric considerations, that the HAT process in **20** and 20H^+ is mediated through the σ^* (Mn–O) orbital, leading to a modest difference in HAT reaction rates.⁸⁵

An interesting disparity was observed in the distribution of products from the oxidation of DHA. At pH 13.4, where the $\text{Mn}^{\text{IV}}(\text{O})_2$ **20** is the main form of the complex, the oxygenated product anthraquinone was the predominant product. In contrast, at pH 4.0, more anthracene was formed, and at even lower pH traces of chlorinated product were identified.^{86,87} The explanation for this was based on different post-HAT reaction pathways: the $\text{Mn}^{\text{III}}\text{--OH}$ derived from **20** can recombine by radical rebound with the substrate, leading to oxygenated products, whereas with $\text{Mn}^{\text{III}}\text{--OH}_2$, produced from 20H_2^{2+} , this is not possible and the radical originating from HAT can diffuse into the solution and react with another molecule of oxidant or a chloride ion present in the buffer solution.

The oxidation of triarylphosphines showed more significant differences in terms of reaction rates;⁸⁸ the reaction of **20** was relatively independent of the presence of electron-withdrawing or -donating substituents on the phosphines, while 20H_2^{2+} was markedly more reactive with electron-rich substrates (Hammett slopes $\rho = -0.08$ and -7.0 respectively); hence, the oxo in **20** was assumed to react by concerted oxygen atom transfer, while the hydroxo in 20H_2^{2+} initiated the oxidation by electron transfer. Moreover, an inverse solvent isotope effect with 20H_2^{2+} suggested the presence of a protonation pre-equilibrium, leading to the formation of the more electropositive oxidant $[\text{Mn}^{\text{IV}}(\text{OH})(\text{OH}_2)(\text{Me}_2\text{EBC})]^{3+}$ (20H_3^{3+}) as the active species.

Iron

A unique example of an $\text{Fe}^{\text{IV}}\text{--OH}$ complex which is capable of hydrocarbon oxidation is $[\text{Fe}^{\text{IV}}(\text{OH})(\beta\text{-BPMCN})(\text{OO}^t\text{Bu})]^{2+}$ (**21**, fig. 1.6).⁹¹ This compound was shown to effect HAT from C–H and O–H bonds, with the hydrogen atom being transferred to the hydroxide rather than the alkylperoxide group. **21** could also be induced to decay through O–O bond scission to form oxoiron(IV) complexes $[\text{Fe}^{\text{IV}}(\text{O})(\beta\text{-BPMCN})(\text{L})]^{2+}$ (**22**, L = CH_3CN or pyridine, fig. 1.6); the oxoiron(IV) complex, in spite of a lower charge displayed greatly

enhanced electrophilic oxidative capabilities as opposed to the hydroxide analogue ($k_2(\mathbf{22} + \text{DHA})/k_2(\mathbf{21} + \text{DHA}) = 100$). This behaviour was attributed, on the basis of DFT calculations, to the disruption of the Fe=O π -bonding, which makes the acceptor orbitals of Fe–OH higher in energy and of lesser O character. KIEs, measured at -70 °C, were also strikingly different with values of 200 for **22** and 3 for **21**.

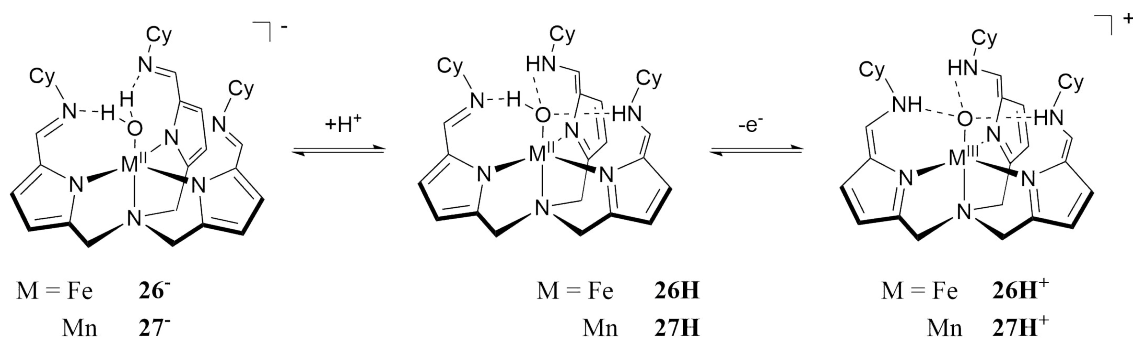
Complexes with second coordination sphere interactions

A class of M–O–X complexes is constituted by those with oxo ligands that are stabilised through a hydrogen bonding network in the second coordination sphere. This approach has been pioneered and widely pursued by Borovik. The tripodal tris-urea ligand H₃buea has been used in order to stabilise a series of M=O and M–OH complexes of both Mn and Fe (**23–24**, fig. 1.6). The ligand possesses three urea groups, each of which can bind the metal through one deprotonated urea N atom, while the second urea NH acts as a hydrogen bond donor. While many of these complexes are best described as possessing terminal oxo ligands, the hydrogen bonding can be thought of conferring a modulation of their properties analogous to those of covalent or coordinative bonding. This is especially relevant for the Mn/Fe^{III} complexes, whose electronic structure is thought to disallow a multiple M=O bond order: delocalisation of the electron density of the highly basic oxo ligand over the H atoms, through hydrogen bonding, is then fundamental in contributing to its stabilisation. As a result, M^{III}–O bonds are elongated with distances closer to those of M–OH complexes than of M=O.

The series of Mn–OH and Mn=O complexes supported by H₃buea spans four oxidation states (Mn^{II/III/IV/V}, fig. 1.6).^{92–100} Amongst them, the Mn=O displayed oxidative reactivity. **23**²⁻ (Mn^{III}–O) abstracted hydrogen atoms from TEMPOH, diphenylhydrazine, DHA and 1,4-cyclohexadiene.⁹⁴ The oxidised form [Mn^{IV}(O)(H₃buea)]⁻ (**23**[•], fig. 1.6), also effected OAT to electron rich phosphines (PPh₂Me and PPhMe₂, but not PPh₃) and HAT from diphenylhydrazine and DHA.^{96,97} BDE_{O–H} for the protonated forms **23H**²⁻ (Mn^{II}–OH), **23H**[•] (Mn^{III}–OH) and **23H** (Mn^{IV}–OH) were estimated to be 77, 89 and 95 kcal/mol respectively.^{93,95,97,98,100} The oxidation of DHA by **23**[•] (Mn^{IV}=O) and **23**²⁻ (Mn^{III}=O) was compared.⁹⁷ Curiously, the Mn^{III} complex reacted faster (**23**²⁻: $k_2 = 0.48 \text{ M}^{-1} \text{ s}^{-1}$, KIE = 2.6; **23**[•]: $k_2 = 0.026 \text{ M}^{-1} \text{ s}^{-1}$, KIE = 6.8), contrary to what was expected on the basis of BDE_{O–H} of the product of this reaction. A mechanism of sequential proton transfer – electron transfer (PT-ET) **23**²⁻, deriving from a more basic oxo ligand, was thus proposed, in contrast with concerted HAT for **23**[•]. Completing the series, the compound [Mn^V(O)(H₃buea)]⁻ (**23**) could abstract a hydrogen atom from 2,4,6-tris-*tert*-butylphenol to give [Mn^{IV}(OH)(H₃buea)]⁻ (**23**[•]).¹⁰⁰

Another $\text{Mn}^{\text{III}}\text{--O--H}$ species, supported by the ligand H_3bupa was isolated as an intermediate in the reduction of dioxygen to water catalysed by a manganese complex.¹⁰¹ **25** (fig. 1.6) could not be unambiguously assigned to either tautomeric structure $[\text{Mn}^{\text{III}}(\text{O})(\text{H}_3\text{bupa})]^-$, or $[\text{Mn}^{\text{III}}(\text{OH})(\text{H}_2\text{bupa})]^-$, *i.e.* the hydrogen atom could either be seen as bound to the oxygen and hydrogen bonding to the pendant ureate arm of the ligand, or vice versa. **25** was capable of abstracting a hydrogen atom from diphenylhydrazine to generate Mn^{II} .

The $\text{Fe}^{\text{III}}\text{--O}$ complex, $[\text{Fe}^{\text{III}}(\text{O})(\text{H}_3\text{buea})]^{2-}$ (**24²⁻**, fig. 1.6)¹⁰² showed in its XRD structure a relatively elongated Fe--O bond (1.81 Å), when compared to Fe=O units, and calculations attributed an Fe--O bond order of one. **24²⁻** was shown to abstract hydrogen atoms from diphenylhydrazine, DHA and 1,4-cyclohexadiene. The reactions were slightly slower than for the Mn equivalent **23²⁻**. The protonated form $[\text{Fe}^{\text{III}}(\text{OH})(\text{H}_3\text{buea})]^-$ (**24H⁻**), was also characterised,⁹⁵ and its $\text{BDE}_{\text{O--H}}$ was determined to be 66 kcal/mol.⁹⁴ The $\text{Fe}^{\text{IV}}\text{=O}$ complex, $[\text{Fe}^{\text{IV}}(\text{O})(\text{H}_3\text{buea})]^-$ (**24⁻**), was formed as the one-electron oxidation product of **24²⁻**. The $S = 1$ product also presents a shortened Fe--O bond, at 1.81 Å; while this is again slightly longer than typical $\text{Fe}^{\text{IV}}\text{=O}$ units, it is more consistent with a double bonded Fe=O structure.¹⁰³ This complex was suggested to decay via HAT from DMF. It was also capable of oxidising diphenylhydrazine. Finally, $[\text{Fe}^{\text{V}}(\text{O})(\text{H}_3\text{buea})]$ (**24**), was postulated to transiently form from one electron-oxidation of **24⁻**, and to abstract hydrogen atoms from either solvent or phenols to give the protonated $[\text{Fe}^{\text{IV}}(\text{O})(\text{H}_4\text{buea})]$ (**24H**).¹⁰⁴



Scheme 1.2. Tautomerism of the tris-pyrrolylamine ligand and interconversion of aquo, hydroxo, and oxo complexes with proton and electron transfer.

Another relevant and analogous ligand system is Fout's tris-pyrrolylamine derivative (sch. 1.2). Each of its three arms can display a tautomerism between an imino-pyrrolide form, which has an anionic N donor and a hydrogen bond acceptor, and an amine-azafulvalene form, which has a neutral N donor and a hydrogen bond donating N-H group. Aquo and hydroxo M^{II} complexes, and oxo M^{III} complexes have been isolated

for both Mn and Fe supported by this ligand (**26** and **27**, sch. 1.2).^{105–107} These complexes were involved in the remarkable catalytic reduction of oxoanions ClO_4^- and NO_3^- to Cl^- and NO respectively, but their oxidative properties have not been reported.^{108,109} The compound **27H** ($\text{Fe}^{\text{III}}=\text{O}$) oxidised diphenylhydrazine, in order to regenerate the Fe^{II} compound **27H**.¹⁰⁹

1.4.3 Lewis acid metal-oxygen adducts

Various simple oxometal complexes from groups VI–VIII of the periodic table are capable oxidants. Interestingly, it has been observed that their reactivity can be greatly enhanced by the addition of Lewis acids (LA), and the formation of electrophilic M–O–LA intermediates was postulated as the explanation. These include compounds such as $\text{K}[\text{Mn}^{\text{VII}}\text{O}_4]$,^{110–112} $(\text{Bu}_4\text{N})_2[\text{Cr}^{\text{VI}}_2\text{O}_7]$ and $(\text{C}_5\text{H}_5\text{NH})[\text{Cr}^{\text{VI}}\text{O}_3\text{Cl}]$,¹¹⁰ $\text{Ba}[\text{Fe}^{\text{VI}}\text{O}_4]$,¹¹³ and $\text{Ba}[\text{Ru}^{\text{VI}}(\text{O})_2(\text{OAc})_4]$,¹¹⁴ and Lewis acids such as Li^+ , Ca^{2+} , Ba^{2+} , Zn^{2+} , Cu^{2+} , Fe^{3+} , Al^{3+} , Sc^{3+} and BF_3 . Evidence for the M–O–LA intermediate was obtained only for the formation of $[\text{MnO}_4\cdot\text{BF}_3]^-$, via stopped-flow spectroscopy.¹¹¹ It oxidised toluene with a reaction rate of $9 \text{ M}^{-1} \text{ s}^{-1}$, which is 7 orders of magnitudes greater than for $[\text{MnO}_4]^-$ alone, but with similar KIEs (6.8 vs. 6). Collins observed a similar effect, in which $[\text{Mn}^{\text{V}}(\text{O})(\text{TAML})]^-$ complexes (TAML = tetraamidomacrocyclic ligands) were activated towards the oxidation of PPh_3 , upon the addition of acidic metal ions.¹¹⁵ The intermediate Mn–O–LA species were nevertheless not observed.

Manganese

The effect of Lewis acid ligation on $\text{Mn}^{\text{IV}}=\text{O}$ complexes has been investigated in several other studies. It was observed that the addition of scandium(III) triflate to the complex $[\text{Mn}^{\text{IV}}(\text{O})(\text{N4Py})(\text{OTf})]^+$ (**28a**), induced stepwise changes in its electronic spectra, corresponding to adducts with one and two equivalents of $\text{Sc}(\text{OTf})_3$ (**28b–c**, fig. 1.7).¹¹⁶ **28b–c** formed with high binding constants ($K_a = 6 \times 10^3 \text{ M}^{-1}$, $K_b \gg 10^4 \text{ M}^{-1}$) and were moderately stable at 25°C ($t_{1/2} = 12\text{h}, 24\text{h}$). This allowed for spectroscopic characterisation, which together with DFT computations confirmed structures with an $\text{Mn}^{\text{IV}}\text{–O–Sc}^{\text{III}}$ core in both compounds, and with the second Sc^{3+} ion in **28c** bound in the second coordination sphere through bridging triflates.

The complex $[\text{Mn}^{\text{IV}}(\text{O})(\text{Bn-TPEN})(\text{OTf})]^{2+}$ (**29a**) displayed entirely similar behaviour, leading to the formation of adducts **29b–c** (fig. 1.7) with respectively one and two Sc^{3+} ions.¹¹⁷ The Sc^{3+} adducts were found to be more reactive than $[\text{Mn}^{\text{IV}}(\text{O})(\text{N4Py})(\text{OTf})]^+$, towards thioanisole ($k_2(\text{28c})/k_2(\text{28a}) = 2200$), but less for HAT reactions ($(k_2(\text{28a})/k_2(\text{28c}))$

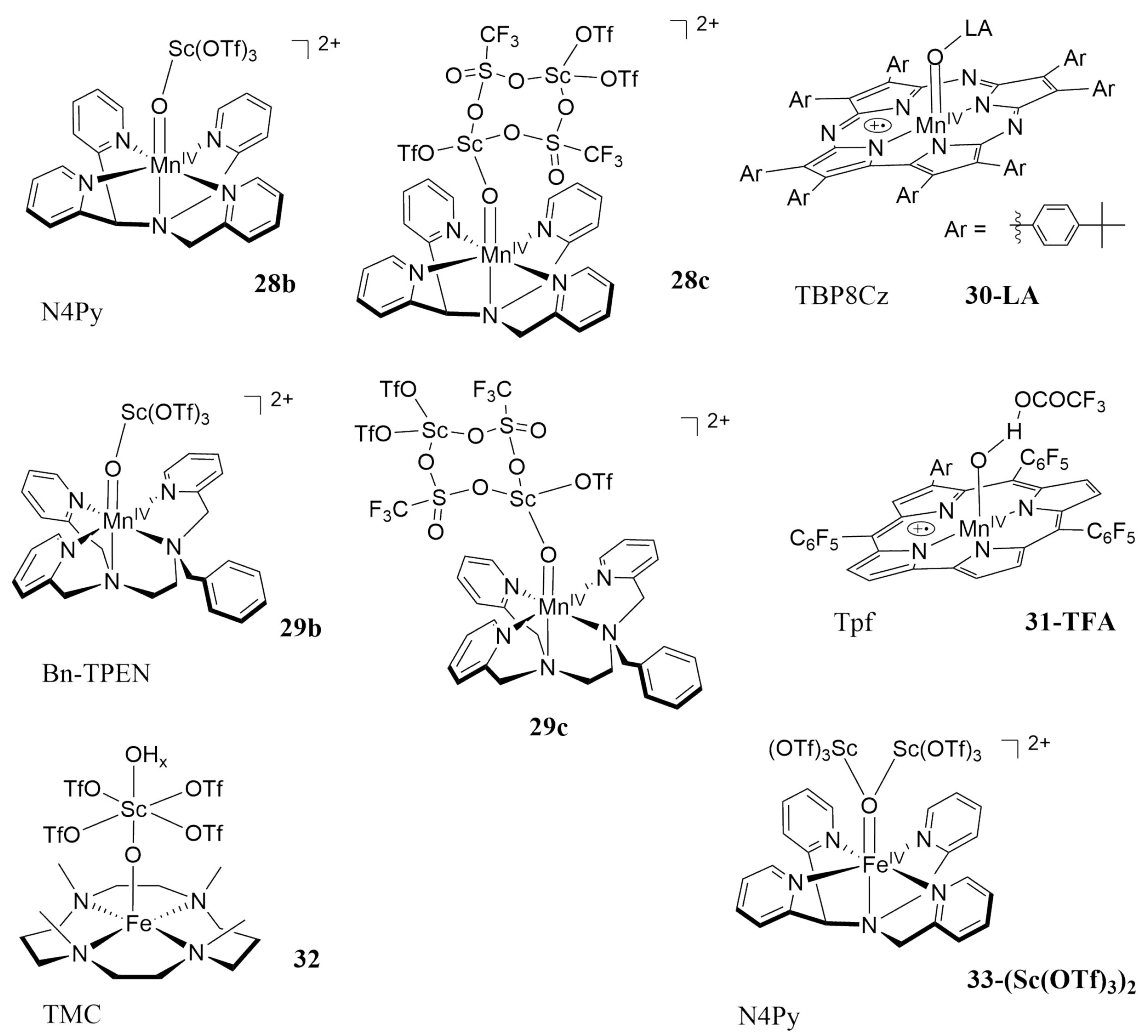


Figure 1.7. Reactive M–O–X complexes of manganese and iron formed as adducts with redox-inactive Lewis acids.

= 5, $k_2(\mathbf{28a})/k_2(\mathbf{28b}) = 180$ for the oxidation of 1,4-cyclohexadiene). The opposite effects were explained by the existence of different mechanisms; the binding of Sc^{3+} greatly increased electrophilicity (E_{red} vs. SCE: $\mathbf{28a} = 0.80$ V, $\mathbf{28b} = 1.31$ V, $\mathbf{28c} = 1.42$ V, $\mathbf{29a} = 0.78$ V, $\mathbf{29b} = 1.28$ V, $\mathbf{29c} = 1.36$ V). Moreover, reduced reorganizational energies were estimated, through Marcus theory, for the Sc^{3+} adducts; possibly, because of the conversion of the $\text{Mn}^{\text{IV}}=\text{O}$ bond to a more elongated $\text{Mn}^{\text{IV}}-\text{O}-\text{Sc}^{\text{III}}$. Together, these effects favoured the switch from direct oxygen atom transfer to the sulfide to a fast electron transfer mechanism. In contrast, the slower HAT reactions were justified on the basis of the increased steric bulk from the $\text{Sc}(\text{OTf})_3$ groups, which hinder the approach of the substrate to the O atom.

The effect of the presence of Lewis acids (Al^{3+} , Sc^{3+} , Y^{3+} , Yb^{3+} , Mg^{2+} , Ca^{2+} , Na^+) on the dihydroxomanganese complex $\mathbf{20H}_2^{2+}$ was also investigated.¹¹⁸ The oxidation of PPh_3 , which occurred via rate determining ET,⁸⁸ was faster by a factor of up to 26, for the trivalent (and more acidic) cations. In contrast, only minor effects on reaction rates were seen in olefin epoxidation and HAT (C–H oxidation) reactions. Still, $\mathbf{20H}_2^{2+} + \text{Al}^{3+}$ could oxidise ethylbenzene ($\text{BDE}_{\text{C-H}} = 85$ kcal/mol). Evidence for the formation of the active intermediates, postulated to possess $\text{Mn}^{\text{IV}}-\text{O}-\text{M}^{\text{n+}}$ structural elements was derived from changes in the UV-Vis. spectra and redox potentials, and in the case of Al^{3+} from the appearance of hyperfine coupling to ^{27}Al ($I = 5/2$) in the EPR spectrum.

An interesting case is that of the complex $[\text{Mn}^{\text{V}}(\text{O})(\text{TBP8Cz})]$ ($\mathbf{30}$), an $\text{Mn}^{\text{V}}=\text{O}$ supported by a porphyrinoid ligand. It was shown that addition of a Lewis acid ($\text{B}(\text{C}_6\text{F}_5)_3$, Zn^{2+} , or H^+) caused the valence tautomerism and the transformation to $[\text{Mn}^{\text{IV}}(\text{O}-\text{LA})(\text{TBP8Cz}^{\bullet+})]$ complexes ($\mathbf{30-LA}$, fig. 1.7), with a ligand radical cation, accompanied by a change from low to high spin state.^{119–121} The reduction potential was found to increase dramatically, with $E_0(\mathbf{30}) = -0.05$ V and $E_0(\mathbf{30-Zn}^{2+}) = +0.69$ vs. SCE.¹²² $\mathbf{30-LA}$ complexes acted as one-electron oxidants (towards ferrocene, phenols, or hydrocarbons), forming $[\text{Mn}^{\text{IV}}(\text{O}-\text{LA})(\text{TBP8Cz})]$, whereas $\mathbf{30}$ acted as a two-electron oxidant, being reduced to $[\text{Mn}^{\text{III}}(\text{OH}_2)(\text{TBP8Cz})]$. The reaction rate towards xanthene was increased by a factor of 4 in $\mathbf{30-Zn}^{2+}$, 10 in $\mathbf{30-H}^+$ and 28 in $\mathbf{30-B}(\text{C}_6\text{F}_5)_3$ (with KIE = 25), as opposed to $\mathbf{30}$.¹²⁰ Thus, in contrast to the examples of $\mathbf{28/29}$, the HAT reactivity of $\mathbf{30}$ was improved by Lewis acids binding. Surprisingly, the oxidation of triarylphosphines followed the opposite trend, with slower rates for $\mathbf{30-LA}$ than for $\mathbf{30}$; showing that while the effect of increased E_0 dominated the one-electron HAT process, the two electrons OAT was inversely affected.¹²²

A close analogue of $\mathbf{30}$, $[\text{Mn}^{\text{V}}(\text{O})(\text{tpf})]$ ($\mathbf{31}$), also displayed tautomerisation on addition of trifluoroacetic acid.¹²³ The product $\mathbf{31-TFA}$ (fig. 1.7), though, was less reactive both

in HAT from phenols and OAT to thioanisole, than **31**. It has been suggested that TFA is only a weak Lewis acid and has limited effect on the electronic properties of the oxidant, together with a small steric inhibition;¹²¹ nevertheless, the reactivity of M–O–LA complexes seems to be governed by very subtle effects.

Iron

Fukuzumi and Nam observed that the electron transfer properties of $[\text{Fe}^{\text{IV}}(\text{O})(\text{TMC})]^{2+}$ changed in the presence of $\text{Sc}(\text{OTf})_3$, and obtained the crystal structure of a complex derived from the reaction (**32**, fig. 1.7).¹²⁴ While originally reported as possessing an $\text{Fe}^{\text{IV}}=\text{O}-\text{Sc}^{\text{III}}-\text{OH}$ core, this description has however been disputed by later computational and spectroscopic studies,^{125,126} which showed that **32** is actually an $\text{Fe}^{\text{III}}-\text{O}-\text{Sc}^{\text{III}}-\text{OH}_2$ complex.

For the iron complex $[\text{Fe}^{\text{IV}}(\text{O})(\text{N4Py})]^{2+}$ (**33**), it was observed that the rate of electron transfer was greatly enhanced in the presence of metal ions (Sc^{3+} , Zn^{2+} , Mg^{2+} , Ca^{2+} ; 108-fold rate enhancement in the case of Sc^{3+}).¹²⁷ This was attributed to a mechanism of metal-coupled electron transfer (in analogy to PCET). According to it, the Lewis acids has a much greater affinity for the $\text{Fe}^{\text{III}}-\text{O}$ moiety, product of the ET reaction, than for the original $\text{Fe}=\text{O}$. Hence, formation of $\text{Fe}^{\text{III}}-\text{O}-\text{LA}$ shifts the equilibrium, providing a larger driving force for the ET reaction. In fact, the $\text{Fe}^{\text{IV}}/\text{Fe}^{\text{III}}$ reduction potential increased by 0.84 V in the presence of two equivalents of $\text{Sc}(\text{OTf})_3$. In contrast to the analogous Mn^{IV} complexes, the Sc^{3+} adducts showed lower stability, and were not isolated and spectroscopically characterised.

An augmentation in reaction rates, and the occurrence of different mechanisms, were also observed in the oxidation of benzyl alcohols, to give aldehydes and dimerised products.¹²⁸ **33**, by itself, abstracted a benzylic hydrogen atom, with KIE = 14; conversely, in the presence of Sc^{3+} the KIE disappeared, and electron transfer (coupled with Sc^{3+} binding) was found to be the rate-determining step in a sequential ET-PT mechanism. The same effects of increased rates, lowered KIE, and switch to an ET rate determining step was observed when the Brønsted acid HClO_4 was added to **33**, in the oxidation of toluene derivatives.¹²⁹ A protonated intermediate was assumed to be the key ET intermediate, although the hydroxo compound $[\text{Fe}^{\text{IV}}(\text{OH})(\text{N4Py})]^{3+}$ (**33H⁺**) was not spectroscopically observed. In later work, the binding of up to two molecules of HOTf (**33**–(**HOTf**)₂ or **33H₂²⁺**) was postulated.¹³⁰

Analogous behaviour was observed in sulfoxidation reactions.^{129,131} While the oxo **33** reacted by concerted OAT, in the presence of either $\text{Sc}(\text{OTf})_3$ or HClO_4 a faster mechanism

of metal-coupled (from **33**–(**Sc**(OTf)₃)_x), or proton-coupled (**33**–**HA**_x) electron transfer arised instead. Enhanced electron transfer was also determined to be at play in the oxidative dimerisation and N-demethylation of *N,N*-dimethylaniline.¹³²

In conclusion, both metal-based Lewis acids and protons appeared to modify oxometal compounds, forming Fe–O–X species with greater propensity to ET reactions; in fact the reaction rates for adducts with HOTf and a series of metal triflates were found to correlate equally well with the same measure of Lewis acidity.¹³³

1.4.4 Late transition M–O–X complexes

When compared to Mn and Fe, the high-valent, reactive complexes of the later transition metals have only recently become a focus of research, and fewer examples of them exist.

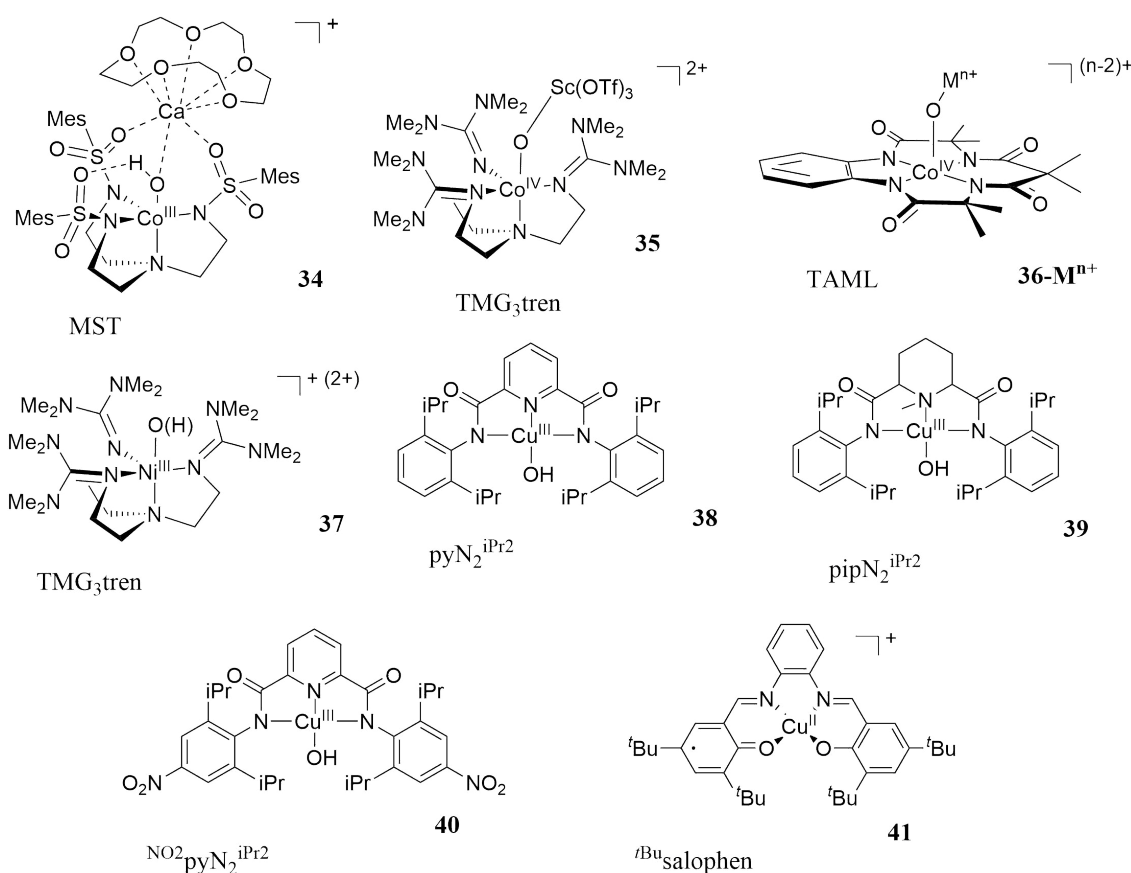


Figure 1.8. High valent M–O–X complexes of Co, Nic, and Cu.

Cobalt

The tris-sulfonamido MST ligand has been used in the preparation of several heterobimetallic complexes. Amongst these, the complex [Co^{III}(μ-OH)(MST)Ca^{II}(15-crown-5)]⁺ (**34**,

fig. 1.8), represents a Co–OH complex, which is capable of oxidising diphenylhydrazine to azobenzene, forming a $\text{Co}^{\text{II}}(\mu\text{-OH}_2)\text{Ca}^{\text{II}}$ product.¹³⁴ **34** possesses an hydroxo ligand that bridges the Co^{III} and Ca^{II} ions, and is further hydrogen bonded to a sulphonamide group's O atom.

Ray has reported a series of Co–O–LA complexes; in contrast to the Fe and Mn examples, the corresponding naked, terminal Co=O haven't been observed, and are presumably not stable species. $[\text{Co}^{\text{IV}}(\text{O})\text{-Sc}(\text{OTf})_3(\text{TMG}_3\text{tren})]^{2+}$ (**35**, fig. 1.8), was obtained from the oxidation of $[\text{Co}^{\text{II}}(\text{OTf})(\text{TMG}_3\text{tren})]^+$ with a iodosoarene in the presence of $\text{Sc}(\text{OTf})_3$.¹³⁵ Borovik has proposed that the characterisation of this species is likely more consistent with a $\text{Co}^{\text{III}}(\mu\text{-OH})\text{-Sc}^{\text{III}}$ structure.¹³⁴ **35** was capable of oxidising PPh_3 , giving PPh_3O and $[\text{Co}^{\text{II}}(\text{OTf})(\text{TMG}_3\text{tren})]^+$, albeit ~ 55 times more slowly than the iron analogue $[\text{Fe}^{\text{IV}}(\text{O})(\text{TMG}_3\text{tren})]^{2+}$. On the other hand, **35**, unlike $[\text{Fe}^{\text{IV}}(\text{O})(\text{TMG}_3\text{tren})]^{2+}$, could oxidise 1,1'-dibromoferrocene, showing a good ET capability. In the oxidation of DHA, as well, a 45% yield of anthraquinone was formed, which is assumed result from ET from DHA rather than HAT.

A similar strategy was utilised to produce the complexes $[\text{Co}^{\text{IV}}(\text{O-M}^{\text{n+}})(\text{TAML})]$ (**36-Mⁿ⁺**, $\text{M}^{\text{n+}} = \text{Sc}^{3+}, \text{Ce}^{3+}, \text{Y}^{3+}, \text{Zn}^{2+}$, fig. 1.8).¹³⁶ $\text{Li}[\text{Co}^{\text{III}}(\text{TAML})].3\text{H}_2\text{O}$ was oxidised either with cerium ammonium nitrate or with an iodosoarene in the presence of metal triflate salts ($\text{Sc}(\text{OTf})_3$, $\text{Ce}(\text{OTf})_3$, $\text{Y}(\text{OTf})_3$, $\text{Zn}(\text{OTf})_2$), giving products with very similar UV-Vis spectra. The putative **36-Sc**, $[\text{Co}^{\text{IV}}(\text{O-Sc}(\text{OTf})_3(\text{OH})_2)(\text{TAML})]^{4+}$, was the most stable of the series and showed oxidation capabilities. It performed HAT from a series of hydrocarbons, including triphenylmethane ($\text{BDE}_{\text{C-H}} = 81 \text{ kcal/mol}$), displaying a Polanyi linear free energy relationship between reaction rates and substrates' $\text{BDE}_{\text{C-H}}$. A KIE of 13 was measured for xanthene, and its product of oxidation xanthone was found, in an isotopic labelling experiment, to incorporate ^{18}O from the Co– ^{18}O –Sc complex **36-Sc**. **36-Sc** also transferred an oxygen atom to arylmethylsulfides, with analogous incorporation of labelled ^{18}O in the resulting sulfoxides. The reaction with para-substituted arylmethylsulfides also showed a Hammett correlation with large negative $\rho = -2.8$, demonstrating the electrophilic character of **36-Sc** in oxygen atom transfer reactions.

Nickel

Ray reported the formation of a mixture of two metastable Ni^{III} moieties, tentatively described as $\text{Ni}^{\text{III}}=\text{O}$ or $\text{Ni}^{\text{III}}\text{-OH}$ compounds (**37**, fig. 1.8), from the reaction of *m*-CPBA acid with $[\text{Ni}^{\text{II}}(\text{OTf})(\text{TMG}_3\text{tren})]^+$.¹³⁷ These were capable of oxidising PPh_3 to PPh_3O , as well as hydrocarbons with weak C–H bonds (including 1,4-cyclohexadiene, $\text{BDE} = 78$

kcal/mol). DHA was oxidised with KIE = 3.9, and there was a Polanyi linear free energy relationship between reaction rates and the hydrocarbon substrates' BDE_{C-H}, which suggest a HAT rate determining step.

Copper

Tolman reported the [Cu^{III}(OH)(pyN₂^{iPr₂})] complex **38** (fig. 1.8), and showed it to be one of the most reactive metal-based HAT reagents known, with reaction rates in the oxidation of DHA of the same order of magnitude, or better than most oxomanganese and iron complexes.^{138,139} With the help of a modified ligand, a complex incorporating a hydroxylated THF molecule was isolated and crystallographically characterised.¹⁴⁰ Extensive studies of **38**, [Cu^{III}(OH)(pipN₂^{iPr₂})] (**39**, fig. 1.8) and [Cu^{III}(OH)(^{NO₂}pyN₂^{iPr₂})] (**40**, fig. 1.8), which respectively possess the more electron-donating ligand pipN₂^{iPr₂}, and the less electron-donating ^{NO₂}pyN₂^{iPr₂}, showed an enhanced reactivity for the electron-poor complexes, as manifested in both reaction rates (k_2 **40/38/39** = 400/38/1) and BDE_{O-H} (**40** = 91, **38** = 90, **39** = 88 kcal/mol).¹⁴¹ Unlike other M–OH and M–OR complexes, these Cu compounds displayed remarkably high kinetic isotope effects (25–30 at –40 °C), together with interesting differences in their dependence from temperature; while not fully understood, these are indicative of subtle effects involving the HAT processes.^{139,141,142} The oxidation of phenols has also been investigated, and showed an apparent switch between a concerted HAT/PCET mechanism to a sequential PT-ET depending on the p*K_a* of the substrates.¹⁴³

A large group of Cu–O–X oxidants is constituted by Cu^{II}(OAr) complexes, which have been designed as models for the active site of galactose oxidase. A peculiarity of these phenoxyl complexes is that the oxidising equivalents are shared between the metal and the radical ligand, each of which is reduced by one electron in the oxidation. Work in the field has been extensively reviewed.^{144–146} These complexes affect the oxidation of aliphatic alcohols to aldehydes, as well as phenols and some hydrocarbons. Some of them displayed high KIEs (e.g., up to 54 for the oxidation of CH₃OH to CH₂O by [Cu^{II}(^tBu₃salophen^{•+})], **41**, fig. 1.8, but 5–10 more commonly), suggesting a HAT rate determining step, with tunnelling behaviour. The reactions are catalytic in the presence of oxygen, implying that the phenolate ligand can be reoxidised, presumably through a Cu–OO[•] intermediate.

1.4.5 Comparative reactivity trends

The oxidising capabilities of M–O–X can be characterised on the basis of certain thermodynamic and kinetic quantities. Activation of C–H bonds occurs generally through HAT,

and the $\text{BDE}_{\text{O-H}}$ of the resulting M-O(H)-X product is a useful measuring stick for comparing reactivity properties. For a kinetic comparison of different oxidants, the reaction by HAT from DHA is a useful benchmark, as it has been extensively investigated for a number of species (table 1.1); for weaker oxidants, the reactivity towards O–H bonds, can be considered instead. The HAT reaction between M-O-X are generally first order in both oxidant and substrates, with k_2 values that span several orders of magnitude (10^{-5} to $10^3 \text{ M}^{-1} \text{ s}^{-1}$ for the oxidation of DHA at 25 °C).

Effects of the central metal

As described above, the BDE of the O–H bonds formed in the oxidant after HAT/PCET are the crucial thermodynamic parameter in determining the reaction's thermodynamics. This $\text{BDE}_{\text{O-H}}$ has been determined for several of the compounds in this review. For Mn/Fe-OH_2 , and $-\text{O(H)R}$ compounds they fall in the 67-89 kcal/mol range. By comparison, for Fe–OH compounds values as high as 99 kcal/mol have been estimated (in compound II of cytochrome P450).¹⁴⁹ Manganese and iron displayed roughly similar levels of reactivity: reaction rates span several orders of magnitude (table 1.1), but are more affected by changes in the coordination environment and supporting ligands than by substituting Fe for Mn. When complexes with the same ligands but different metals were compared (e.g. **6/7**, **17/18**, **24²⁻/23²⁻**), Mn had slightly higher reaction rates, consistent with correspondingly higher $\text{BDE}_{\text{O-H}}$ and E_0 values. With the exception of the highly charged $\text{Fe}^{\text{III}}\text{-OH}$ complex **13**, Co^{IV} and Cu^{III} complexes **36–Sc** and **38–40** surpass Fe–OX and Mn–OX reactivity by orders of magnitude in the oxidation of DHA, and compare favourably with many M=O complexes. Tolman's $\text{Cu}^{\text{III}}\text{-OH}$ species, in particular, displayed almost record k_2 values ($2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$), accompanied by higher $\text{BDE}_{\text{O-H}}$ values of 88-91 kcal/mol, and were capable of oxidising unactivated C–H bonds such as those of cyclohexane ($\text{BDE}_{\text{C-H}} = 99 \text{ kcal/mol}$).¹³⁹ The M-O-X intermediates deriving from the late transition metals can be thus considered intriguing species, which are capable of remarkable reactivity.

Effects of the O–X ligands

As mentioned above, the nature of the O–X ligand has often greater effect than that of the central metal, even leading to the variation in reaction mechanism. The group of complexes with ligands such as terminal hydroxide, alkoxide and simple acid oxoanions showed largely similar behaviours. They perform C–H and O–H bond activation through HAT, as demonstrated by KIEs and Polanyi linear relationships, and their reactivity is modulated by steric and inductive electronic effects. For example, $\text{Fe}^{\text{III}}\text{-OH}$ (**6**) displayed

Table 1.1. Kinetic and thermodynamic parameters for M–O–X compounds that have been studied in the oxidation of C–H and O–H bonds.

Compound	$k_2 / \text{M}^{-1} \text{s}^{-1} (\text{T} / ^\circ\text{C})$ [a]	KIE (T / °C) [a]	$\Delta^\ddagger H /$ kcal/mol	$\Delta^\ddagger S / \text{cal}$ $\text{K}^{-1} \text{mol}^{-1}$	BDE _{O–H} / kcal/mol [b]	E_0 vs SHE / V	$\Delta^\ddagger G$ / $\Delta(BDE)$ slope [c]	Reference
5	1.2×10^{-4} (25)	5.5 (25)	13.4	-25	83.5	0.660	0.17	65,147
6	4.3×10^{-4} (25)	6.3 (25)	13.2	-26	80	0.555	0.26	69
7	1.6×10^{-3} (25)	2.4 (25)	9.3	-36	82	0.810	0.07	68
8	-	1.7 (25, ascorbate)	-	-	77	0.60 [e] at pH 2	-	70
9	9.8×10^{-4} (50)	5.1 (50)	-	-	-	0.903 irr.	-	71
10	-	-	-	-	-	0.900 irr.	-	71
11a	1.6×10^{-4} (60)	1.9 (60)	-	-	-	0.79	-	72
13	73 [d]	21 (20) [d]	6.8	-27.2	84	1.09 [f] at pH 2	-	74
20	2.21×10^{-3} (25)	2.6 (25)	13.7	-24.5	-	-	0.16	82–90
20H₂²⁺	3.51×10^{-5} (25)	4.8 (25)	15.2	-27.9	83.0	0.756	0.14	82–90
20H⁺	6.64×10^{-4} (25)	-	-	-	84.3	-	0.23	82–90
21	1.5×10^{-3} (-70)	3 (-70)	-	-	-	-	-	91
22	0.14 (-70)	200 (-70)	-	-	-	-	-	91
23²⁻	0.29 [d]	2.6 (20)	14	-14	77	0.564 [g] irr.	-	93–95
23⁻	2.6×10^{-2} [d]	6.8 (20)	5	-49	89	-0.36 [g] irr.	-	96,97
24²⁻	-	-	-	-	66	0.98 [g] irr.	-	93,102
30	1.8×10^{-5} (23)	-	-	-	-	0.19 [e]	-	119–121,148
30–Zn	-	-	-	-	-	0.93 [e]	-	119–121,148
30–H	6.7×10^{-4} (23)	-	-	-	-	-	-	120
30–B(C₆F₅)₃	4.3×10^{-4} (23)	25 (xanthene)	-	-	-	-	-	120
36–Sc	0.21 (5)	13 (5, xanthene)	-	-	-	-	0.30	136
37	1.25×10^{-2} (-30)	3.9 (-30)	-	-	-	-	-	137
38	1.9×10^2 (25) [d]	29 (-40)	5.1	-31	90	0.566 [g]	0.37	138,141
39	5.0 (25) [d]	25 (-40)	3.8	-38	88	0.380 [g]	-	141
40	2×10^3 (25) [d]	26 (-40)	4.9	-27	91	0.764 [g]	-	141
12	76 (25, TEMPOH)	-	-	-	67	-0.83	-	73
14	0.13 (25, TEMPOH)	1.8 (25)	9.9	-35	-	-0.02 [g]	0.08	75,77
15	3.9 (-35, TEMPOH)	2.7 (-35)	5.7	-41	-	-0.15 [g]	-	75,77
16	8×10^{-2} (25, TEMPOH)	1.8 (25)	11.4	-27	-	-0.24 [g] irr.	0.20	76
17	2.1×10^3 (25, TEMPOH)	2.1 (25)	8.2	-25.5	70.1 [h]	-0.02 [g]	-	79
17b	3.6×10^2 (25, TEMPOH)	3.1 (25)	8.3	-29	-	0.13 [g]	-	78
18	-	-	-	-	68.6 [h]	-0.254	-	79
19	11.7 (-70, 2,6-DTPB)	5.3 (-70, 2,6-DTPB)	-	-	-	-	0.63	80,81
19H⁺	1.9×10^{-3} (-70, 2,6-DTPB)	9.5 (-70, 2,6-DTPB)	-	-	-	1.46 [g]	0.36	80,81

[a] k_2 and KIE refer to the oxidation of DHA unless otherwise specified. [b] BDE of the newly formed O–H bond after HAT. [c] Bell-Evans-Polanyi slopes were calculated from reported kinetic data; the Eyring equation was used to derive activation energies. [d] Data at 25 °C was not available; values were derived from the experimentally determined activation parameters via the Eyring equation. [e] Corrected based on SCE = 0.24 V vs. SHE. [f] Corrected based on AgCl = 0.23 vs. SHE. [g] Corrected based on Fc = 0.64 V vs. SHE. [h] Bond dissociation free energies are reported instead of BDEs.

slightly faster reaction rates, compared to $\text{Fe}^{\text{III}}\text{--OCH}_3$ (**5**), in spite of both lower product $\text{BDE}_{\text{O--H}}$ and E_0 . This was attributed to lower steric impediments for the hydroxide complex versus the methoxide. Similarly, $\text{Mn}^{\text{III}}\text{--OH}$ complexes **14** and **17a** were more reactive than their counterpart $\text{Mn}^{\text{III}}\text{--OCH}_3$ (**16** and **17b**). Aryloxide ligands, on the other hand, did not produce reactive complexes in **17c,d**. Varying the chain length of linear alkoxide ligands (C1-C4) did not induce a large effect in reactivity differences in **11a-d**. Interestingly, the order of oxidising power in the series **17a-d** (and in **5,6**) is the reverse of their reduction potential.

Oxo versus O–X ligands

It is interesting to compare the structure and reactivity of M--O--X complexes to that of terminal M=O complexes. A structural feature that is crucial in determining the reactivity properties of M=O complexes is π bonding between the O-atom and the metal. The O^{2-} ligand is a strong π donor, which generates destabilising interactions with occupied d orbitals (section 1.3.1). By contrast, in an $\text{O}^-\text{--X}$ ligand the electron density is relieved by the formation of the O--X bond. Although one electron pair can still be available for π donation to the metal, the $\text{O}^-\text{--X}$ ligands are not obligate π donors, leading to more subtle effects in bonding and reactivity. In their oxidising reactions, the general trend is for M=O complexes to show a strong preference for the concerted group transfer mechanisms. For M--O--X this preference is less marked. Protonation or Lewis acid binding cause increased charge and E_0 , improving the driving force for ET. As a result the mechanisms can switch to either sequential ET-PT, ET followed by diffusion of the resulting substrate radical cation, or concerted PCET, but with a bigger effect of electron transfer on the reaction rates. In the systems that allow the direct comparison of --OH and =O species supported by the same ligands, the M=O were markedly more reactive ($k_2(\mathbf{19})/k_2(\mathbf{19H}^+) = 6000$; $k_2(\mathbf{20})/k_2(\mathbf{20H}_2^{2+}) = 60$; $k_2(\mathbf{22})/k_2(\mathbf{21}) = 90$), although some M--O--X complexes, particularly the tetracationic $\text{Fe}^{\text{III}}\text{--OH}$ **13** and the Co^{IV} and Cu^{III} complexes **36–Sc** and **38–40** can rival or surpass them.

Effects of Lewis acid ligation

A wider variety of mechanisms is involved in the oxidations performed by M--O--LA complexes. An important factor is that these highly electron-withdrawing groups tend to lead to particularly high reduction potentials. Reactions which occur through rate determining electron transfer are then more favoured, especially as concerted group transfer reactions (HAT/PCET and OAT) can suffer from steric hindrance. Such effects were observed in the

Mn compounds **20H₂²⁺-LA**, which was faster than the corresponding M=O and M-OH compounds in ET-initiated oxidation of phosphines, but slower in OAT to alkenes and HAT; in **28b-c**, which were faster than **28a** in ET to sulphides, but slower in HAT reactions; and in the iron compound **33**, which switched from HAT to ET-PT in benzylic oxidations in the presence of Sc³⁺. In the latter case, the large increase of E_0 induced upon binding of the Sc³⁺, without a corresponding increase of the pK_a , even caused the favoured mechanism in the oxidation of C-H bonds to tip from concerted PCET to a sequential ET-PT, with rate determining electron transfer processes, as evidenced by the disappearance of a KIE.

Effects of the supporting ligands

The supporting, spectator ligand also plays an important role: in general, the complexes with more electron-poor ligands were more capable HAT reagents. In fact, both lipoygenase and its functional models (**5-11**) have uncommonly high Fe^{III/II} redox potentials (>0.55 V vs. SHE). Neutral ligands tend to give better performances than anionic ones; the uncharged **12**, with $E_0 = -0.83$ V, had only limited oxidation capability (reacted with the weak O-H bond of TEMPOH). The porphyrinoid systems **12** (neutral) and **13** (charge +4, arising from N-methylpyridinium moieties at the periphery of the ligand) demonstrate the dramatic effect that a change in electron-poorness of the system has on its oxidation power. In the series of Cu^{III} complexes **38-40**, as well, the more electron-rich ligands corresponded to lower E_0 , BDE_{O-H}, and reaction rates. It should be remembered that E_0 is the relevant thermodynamic parameter only for a simple electron transfer process, while the BDE is the crucial parameter in defining a PCET/HAT reaction. E_0 and pK_a concur in determining the BDE of an O-H bond, and the two are somewhat inversely correlated. The significant influence of E_0 in the HAT reactivity of M-O-X species can be attributed to a limited variability of pK_a : the basicity of -O-X is not as strongly affected by the electron density of the metal as that of the terminal oxo ligand in M=O is, as a consequence of π bonding. Experimentally determined BDE_{O-H} values are only available for a few complexes, which unfortunately limits the understanding of these effects.

Kinetic isotope effects

An important feature of the HAT reactions is that they display primary KIEs when deuterated substrates are oxidised, as expected when C-H (C-D) bond breaking is involved in the rate determining step. The KIE values for the M-O-X compounds are relatively small (<<10), with few exceptions which are represented by the highly reactive **13** (KIE

= 21) and **38-40** (KIEs = 25-29), and the triarylboron adduct **30-B(C₆F₅)₃** (KIE = 25). These observations are in sharp contrast with very high values observed in M=O complexes; Fe^{IV}=O complex **22** has KIE = 200 at -70 °C ($k_2 = 0.14 \text{ M}^{-1} \text{ s}^{-1}$), while Fe^{IV}-OH **21**, supported by the same ligand, has only KIE = 3 ($k_2 = 0.0015 \text{ M}^{-1} \text{ s}^{-1}$). Interestingly, theoretical studies have failed to predict a large difference in KIEs between Fe^{IV}=O and Fe^{IV}-OH.¹⁵⁰ According to its semiclassical derivation, an H/D KIE arises from the difference in zero-point energies of the stretching vibrations in the E-H bond that is broken (1.15 kcal/mol higher in C-H vs C-D). In the transition state of an HAT reaction, this vibration is lost, and the original ΔE translates to a lower activation energy for C-H breaking than for C-D.^{151,152} Values of KIE lower than those thereby predicted (~7 at room temperature) are however not uncommon. A possible cause is a lack of linearity in the O---H---C transition state. It is possible that this might be more common for M-O-X type oxidants, whose stereoelectronic properties are more likely to promote an approach along a narrower angle than 180°, resulting in low KIE values. The very large KIEs observed in M=O however result from tunnelling effects, which complicates the treatment of the phenomenon; the factors affecting their exact magnitude are as of yet not completely understood.

Conclusions

In conclusion, numerous high valent M-O-X species have been investigated as oxidising intermediates, and they are competent in reactions that include the activation of hydrocarbons through HAT. M-O-X complexes of the late transition metals seem to be promising oxidants, rivalling some of the better known M=O complexes. Numerous steric and electronic effects have been shown to affect their reactivity, often leading to subtle mechanistic variations. In general, when compared to M=O, several complexes have shown a relatively higher propensity to undergo electron transfer processes, as opposed to concerted atom transfer (HAT, OAT), presumably as a consequence of higher charge and reduction potentials. Nevertheless, many of these effects are still poorly understood, due to the difficulty of drawing general trends from limited examples. Several, relatively unexplored new directions of research are thus open in the study of reactive M-O-X complexes, and will hopefully lead to new strategies towards the development of efficient catalysts for the oxidation of hydrocarbons.

1.5 Nickel-based oxidations

1.5.1 Enzymes and synthetic catalysts

In contrast to metals such as manganese, iron and copper, nickel is less common in biological systems, and only a few Ni-dependent enzymes are known.¹⁵³ Aciredutone dioxygenase catalyses the oxidation of aciredutone to 3-(methylthio)propionate, but the role of the metal is limited to that of a Lewis acid.¹⁵⁴ Quercetin 2,4-dioxygenase activates oxygen and initiates the aerobic degradation of quercetin, although it hasn't been established whether the metal is redox-active in the reaction.¹⁵⁵ It has been suggested that nickel it has been rarely selected for by evolution because it easily substitutes Fe in certain DNA-repairing enzymes, making it potentially toxic.¹⁵³ Moreover, the aqueous Ni^{II} ion is redox-inactive, as both its oxidation and reduction occur at more extreme potentials than those of water; electronic modulation by the ligands is thus highly important. On the other hand, it possesses a flexible coordination geometry, as octahedral, square-planar and tetrahedral complexes of Ni^{II} are all common, unlike for heavier d^8 ions.¹⁵⁶

In contrast with this limited biological utilisation, numerous homogeneous and heterogeneous nickel oxidation catalysts exist. In the 80s and 90s, alkene epoxidation catalysts were developed, based on various N, O and P ligated Ni^{II} salts.^{157–160} Kochi and Burrows conducted independent mechanistic studies which led to the suggestion of $\text{Ni}^{\text{IV}}=\text{O}$ as the OAT agent, on the basis of the analysis of product distribution and of side reactions; the species was never observed.^{161,162} Computational studies have also suggested $\text{Ni}^{\text{IV}}-\text{OH}$ type species capable of epoxidation.¹⁶³ In the epoxidation reactions, competitive ligand and solvent oxidations have been observed, which would proceed through HAA, hinted at the possibility for hydrocarbon oxidation. More recently, this has been achieved catalytically with Ni^{II} complexes supported by various tetradentate polypyridylamine ligands by Itoh's and Palanandaviar's groups.^{164–168} Both $\text{Ni}^{\text{III}}=\text{O}$ and $\text{Ni}^{\text{IV}}=\text{O}$ intermediates have been proposed on the basis of computational studies.¹⁶⁹ A nickel(II)-acylperoxo complex was also isolated, and proposed as an alternative oxidant in catalysts supported by hydrotris(pyrazolyl)borate type ligands.¹⁷⁰ Itoh's catalysts were also shown to oxidise arenes selectively to phenols; in this case dinuclear dinickel(III)-bis(μ -oxo) complexes were proposed as the active metal species.¹⁷¹ Water oxidation catalysis by nickel complexes has also been demonstrated.^{172,173} Finally, the chlorination of hydrocarbons, by NaOCl and under nickel catalysis, has been demonstrated, although mechanistic studies in this case pointed towards the formation of highly reactive, metal-free $\text{Cl}^\bullet$ radicals.¹⁷⁴

1.5.2 Model complexes

As the work done in catalysis shows, a multitude of reactions and mechanisms involving high-valent nickel have been observed or hypothesised. Model complexes for the hypothesised intermediates are a rich area of study. Several structural motifs have been explored and structurally characterised, including Ni-peroxo, -superoxo, -alkylperoxo and -acylperoxo.¹⁷⁵ Moreover, binuclear compounds with bridging oxo ligands ($[\text{Ni}^{\text{III}}_2(\mu\text{-O})_2]$,^{176–181} and $[\text{Ni}^{\text{III}}(\mu\text{-O})_2\text{Cu}^{\text{III}}]$ ³⁸) have been found to be effective both as electrophilic (HAT, aromatic oxidation) and nucleophilic (aldehyde deformylation) oxidants.

In contrast, terminal Ni-O complexes present a much more limited number of examples; these include the putative $\text{Ni}^{\text{III}}\text{-O}^\bullet$ and $\text{Ni}^{\text{III}}\text{-O(H)}$ species (see **3**, section 1.3.2 and **37**, section 1.4.4). Another highly reactive, metastable species, with a proposed $\text{Ni}^{\text{IV}}\text{-OCl}$ structure has been recently reported (**42**); **42** was capable of epoxidising alkenes and hydroxylating alkanes (cyclohexane), at even faster rates than the $\text{Ni}^{\text{III}}\text{-O}^\bullet$ analogue **3**.¹⁸² Aside from these, a few unreactive Ni-OX species are known. Latos-Grażyński obtained a complex, from the addition of hydroxide to a bromo Ni^{III} species, which was only characterised by EPR spectroscopy.¹⁸³ Liaw reported $\text{Ni}^{\text{III}}\text{-OCH}_3$ and $\text{Ni}^{\text{III}}\text{-OPh}$ species, but didn't investigate their reactivity.¹⁸⁴ Finally, organometallic $\text{Ni}^{\text{III}}\text{-OR}$ complexes have been prepared which can reductively eliminate to form C-O bonds.¹⁸⁵ The limited number of examples demonstrate how the difficulty of trapping highly reactive, terminal Ni-O species has hindered the progress towards a better understanding of their structure and reactivity, and their catalytic behaviour.

1.6 Aims & methods

The overarching aim of my group's research is the preparation of high-valent metal-oxygen complexes, which can function as models of the intermediates that are hypothesised to activate C-H bonds in catalytic systems. Nickel was chosen as the main focus of this project, with the ultimate goal of isolating the terminal oxo complexes, $\text{Ni}^{\text{III}}\text{=O}$ or $\text{Ni}^{\text{IV}}\text{=O}$; as well as other $\text{Ni}^{\text{III}}\text{-O-X}$ species. Trapping these species will help elucidate their role in catalytic cycles, and ascertain how their oxidising power and mechanism of action compare with those of the better-understood Fe and Mn equivalents.

The first step in the investigation is the synthesis and characterisation of stable, low-valent (Ni^{II}) precursors, through the ordinary methods of coordination chemistry. The pyridinedicarboxamidato(2-) ligands were selected as ideal frameworks for the stabilisation of the high oxidation states of nickel (fig. 1.9). The anionic amidate donors, due

to their strong σ -donating ability, are capable of stabilising high oxidation states of the central metal; these moieties are also resistant to oxidative and hydrolytic degradation.¹⁸⁶ Moreover pincer ligands, that is, tridentate, meridionally coordinating ligands, are capable of favouring the square planar geometry, which, based on the arguments exposed in section 1.3.1, helps stabilise the π -donating O ligands. A further advantage of pincer ligands that contributes to their widespread use in catalysis is that their conformational rigidity makes them highly resistant to several common degradation pathways.^{187,188} Tolman made use of *N,N'*-bis(2,6-diisopropylphenyl)-2,6-pyridinedicarboxamidato(2-) ($\text{pyN}_2^{\text{iPr}_2}$) and similar ligands to prepare the $\text{Cu}^{\text{III}}\text{-OH}$ compounds **38-40**,^{138,141} as well as an analogous $\text{Cu}^{\text{II}}\text{-O}_2^{\bullet}$.¹⁸⁹ Thermally stable Ni^{III} and Ni^{IV} species have also been synthesised as 2:1 $\text{pyN}_2^{\text{H}_2}$: Ni complexes.¹⁹⁰

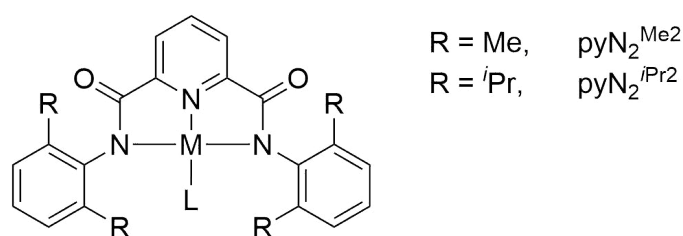


Figure 1.9. Complexes of the ligands $\text{pyN}_2^{\text{Me}_2}$ and $\text{pyN}_2^{\text{iPr}_2}$.

Once the Ni^{II} precursors are synthesised, high-valent species can then be generated through their chemical oxidation. Metastable intermediates can be trapped by the use of low-temperature techniques, and studied spectroscopically (UV-visible, vibrational, EPR, NMR spectroscopies); in the case of highly reactive species, only possessing a transient existence, indirect evidence can still be derived from the analysis of reaction products and reaction kinetics.

Aside from their structural and spectroscopic properties, a central focus is on the reactivity of the intermediates, specifically in oxidation reactions. The main modes of reactivity is expected to correspond to those familiar from enzymes and Fe/Mn models (section 1.2): chiefly HAT, from both C–H and O–H bonds, and OAT; reaction with model substrates and kinetic analysis is an effective way of investigating these reactions. Two fundamental questions revolve around the individuation of structure/reactivity relationships. A first goal is to determine the effects that the increased *d* electron count and electronegativity in moving from the middle to the right of the transition series, have on the oxidising power of the complexes and their feasibility as intermediates in catalytic systems. At the same time,

comparing systems with the same central metal, it would be interesting to assessing how oxo complexes differ from those having different terminal O-donor ligands, in terms of both oxidising power and variation in their mechanisms of formation and reactivity. The results in this field of investigation will be beneficial to the understanding and design of oxidation catalysts.

References

- (1) Doble, M. V.; Ward, A. C. C.; Deuss, P. J.; Jarvis, A. G.; Kamer, P. C. J. *Bioorg. Med. Chem.* **2014**, *22*, 5657–5677.
- (2) Arakawa, H. et al. *Chem. Rev.* **2001**, *101*, 953–996.
- (3) Que, L.; Tolman, W. B. *Nature* **2008**, *455*, 333–340.
- (4) Ray, K.; Pfaff, F. F.; Wang, B.; Nam, W. *J. Am. Chem. Soc.* **2014**, *136*, 13942–13958.
- (5) Mirica, L. M.; Klinman, J. P. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 1814–1819.
- (6) Torres Pazmino, D. E.; Winkler, M.; Glieder, A.; Fraaije, M. W. *J. Biotechnol.* **2010**, *146*, 9–24.
- (7) Peck, S. C.; van der Donk, W. A. *Curr. Opin. Chem. Biol.* **2013**, *17*, 580–588.
- (8) Roach, P. L.; Clifton, I. J.; Hensgens, C. M.; Shibata, N.; Schofield, C. J.; Hajdu, J.; Baldwin, J. E. *Nature* **1997**, *387*, 827–830.
- (9) Groves, J. T.; Haushalter, R. C.; Nakamura, M.; Nemo, T. E.; Evans, B. J. *J. Am. Chem. Soc.* **1981**, *103*, 2884–2886.
- (10) Penner-Hahn, J. E.; McMurry, T. J.; Renner, M.; Latos-Grażyński, L.; Eble, K. S.; Davis, I. M.; Balch, A. L.; Groves, J. T.; Dawson, J. H.; Hodgson, K. O. *J. Biol. Chem.* **1983**, *258*, 12761–12764.
- (11) Penner-Hahn, J. E.; Smith Eble, K.; McMurry, T. J.; Renner, M.; Balch, A. L.; Groves, J. T.; Dawson, J. H.; Hodgson, K. O. *J. Am. Chem. Soc.* **1986**, *108*, 7819–7825.
- (12) Rohde, J. U.; In, J. H.; Lim, M. H.; Brennessel, W. W.; Bukowski, M. R.; Stubna, A.; Munck, E.; Nam, W.; Que L., J. *Science* **2003**, *299*, 1037–1039.
- (13) Que, L. *Acc. Chem. Res.* **2007**, *40*, 493–500.
- (14) Nam, W. *Acc. Chem. Res.* **2007**, *40*, 522–531.
- (15) McDonald, A. R.; Que, L. *Coord. Chem. Rev.* **2013**, *257*, 414–428.
- (16) Sono, M.; Roach, M. P.; Coulter, E. D.; Dawson, J. H. *Chem. Rev.* **1996**, *96*, 2841–2888.
- (17) Meunier, B.; de Visser, S. P.; Shaik, S. *Chem. Rev.* **2004**, *104*, 3947–3980.
- (18) Nam, W.; Lee, Y.-M.; Fukuzumi, S. *Acc. Chem. Res.* **2014**, *47*, 1146–1154.
- (19) Warren, J. J.; Tronic, T. A.; Mayer, J. M. *Chem. Rev.* **2010**, *110*, 6961–7001.
- (20) Mayer, J. M. *J. Phys. Chem. Lett.* **2011**, *2*, 1481–1489.
- (21) Bell, R. P. *Proc. Roy. Soc. London Ser. A* **1936**, *154*, 414–429.
- (22) Evans, M. G.; Polanyi, M. *T. Faraday Soc.* **1938**, *34*, 11–24.
- (23) Bordwell, F. G.; Cheng, J. P.; Harrelson, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 1229–1231.
- (24) Shaik, S.; Hirao, H.; Kumar, D. *Acc. Chem. Res.* **2007**, *40*, 532–542.
- (25) Usharani, D.; Janardanan, D.; Li, C.; Shaik, S. *Acc. Chem. Res.* **2013**, *46*, 471–482.
- (26) Srnc, M.; Wong, S. D.; England, J.; Que, L.; Solomon, E. I. *Proc. Natl. Acad. Sci. U.S.A.* **2012**, *109*, 14326–14331.
- (27) Ye, S.; Neese, F. *Proc. Natl. Acad. Sci. U.S.A.* **2011**, *108*, 1228–1233.
- (28) Roth, J. P.; Lovell, S.; Mayer, J. M. *J. Am. Chem. Soc.* **2000**, *122*, 5486–5498.
- (29) Roth, J. P.; Yoder, J. C.; Won, T.-J.; Mayer, J. M. *Science* **2001**, *294*, 2524–2526.
- (30) Mayer, J. M. *Acc. Chem. Res.* **2011**, *44*, 36–46.
- (31) Luo, Y., *Handbook of Bond Dissociation Energies in Organic Compounds*; Taylor & Francis: 2002.
- (32) De Visser, S. P.; Shaik, S. *J. Am. Chem. Soc.* **2003**, *125*, 7413–7424.
- (33) De Visser, S. P.; Oh, K.; Han, A.-R.; Nam, W. *Inorg. Chem.* **2007**, *46*, 4632–4641.
- (34) Honda, K.; Cho, J.; Matsumoto, T.; Roh, J.; Furutachi, H.; Tosha, T.; Kubo, M.; Fujinami, S.; Ogura, T.; Kitagawa, T.; Suzuki, M. *Angew. Chem. Int. Ed.* **2009**, *48*, 3304–3307.
- (35) Lehnert, N.; Fujisawa, K.; Solomon, E. I. *Inorg. Chem.* **2003**, *42*, 469–481.
- (36) Mehn, M. P.; Fujisawa, K.; Hegg, E. L.; Que, L. *J. Am. Chem. Soc.* **2003**, *125*, 7828–7842.
- (37) Cho, J.; Sarangi, R.; Nam, W. *Acc. Chem. Res.* **2012**, *45*, 1321–1330.
- (38) Kundu, S.; Pfaff, F. F.; Miceli, E.; Zaharieva, I.; Herwig, C.; Yao, S.; Farquhar, E. R.; Kuhlmann, U.; Bill, E.; Hildebrandt, P.; Dau, H.; Driess, M.; Limberg, C.; Ray, K. *Angew. Chem. Int. Ed.* **2013**, *52*, 5622–5626.
- (39) Gunay, A.; Theopold, K. H. *Chem. Rev.* **2010**, *110*, 1060–1081.
- (40) Pierpont, A. W.; Cundari, T. R. *Inorg. Chem.* **2010**, *49*, 2038–2046.

- (41) Gherman, B. F.; Tolman, W. B.; Cramer, C. J. *J. Comput. Chem.* **2006**, *27*, 1950–1961.
- (42) Shiota, Y.; Yoshizawa, K. *J. Am. Chem. Soc.* **2000**, *122*, 12317–12326.
- (43) Schröder, D.; Holthausen, M. C.; Schwarz, H. *J. Phys. Chem. B* **2004**, *108*, 14407–14416.
- (44) Roithová, J.; Schröder, D. *Chem. Rev.* **2009**, *110*, 1170–1211.
- (45) Ballhausen, C. J.; Gray, H. B. *Inorg. Chem.* **1962**, *1*, 111–122.
- (46) Winkler, J. R.; Gray, H. B. *Struct. Bond.* **2012**, *142*, 17–28.
- (47) Hay-Motherwell, R. S.; Wilkinson, G.; Hussain-Bates, B.; Hursthouse, M. B. *Polyhedron* **1993**, *12*, 2009–2012.
- (48) Cundari, T. R.; Conry, R. R.; Spaltenstein, E.; Critchlow, S. C.; Hall, K. A.; Tahmassebi, S. K.; Mayer, J. M. *Organometallics* **1994**, *13*, 322–331.
- (49) Poverenov, E.; Efremenko, I.; Frenkel, A. I.; Ben-David, Y.; Shimon, L. J. W.; Leitun, G.; Konstantinovskii, L.; Martin, J. M. L.; Milstein, D. *Nature* **2008**, *455*, 1093–1096.
- (50) Corona, T.; Pfaff, F. F.; Acuña-Parés, F.; Draksharapu, A.; Whiteoak, C. J.; Martin-Diaconescu, V.; Lloret-Fillol, J.; Browne, W. R.; Ray, K.; Company, A. *Chem. Eur. J.* **2015**, *21*, 15029–15038.
- (51) Wang, B. et al. *Nat. Commun.* **2017**, *8*, Article number: 14839.
- (52) Andreou, A.; Feussner, I. *Phytochemistry* **2009**, *70*, 1504–1510.
- (53) Ivanov, I.; Heydeck, D.; Hofheinz, K.; Roffeis, J.; O'Donnell, V. B.; Kuhn, H.; Walther, M. *Arch. Biochem. Biophys.* **2010**, *503*, 161–174.
- (54) Schneider, C.; Pratt, D. A.; Porter, N. A.; Brash, A. R. *Chem. Biol.* **2007**, *14*, 473–488.
- (55) Fukuzumi, S. *Helv. Chim. Acta* **2006**, *89*, 2425–2440.
- (56) McGinley, C. M.; van der Donk, W. A. *Chem. Commun.* **2003**, *23*, 2843–2846.
- (57) Hamberg, M.; Su, C.; Oliw, E. H. *J. Biol. Chem.* **1998**, *273*, 13080–13088.
- (58) Su, C.; Sahlin, M.; Oliw, E. H. *J. Biol. Chem.* **2000**, *275*, 18830–18835.
- (59) Wennman, A.; Karkehabadi, S.; Oliw, E. H. *Arch. Biochem. Biophys.* **2014**, *555*, 9–15.
- (60) Whittaker, J. W. In *Metal Ions In Biological Systems*, Siegel, H. S., A, Eds.; Marcel Dekker, Inc.: New York, 1994; Vol. 30, pp 315–360.
- (61) Whittaker, J. W. *Chem. Rev.* **2003**, *103*, 2347–2364.
- (62) Mandal, S. K.; Que, L. *Inorg. Chem.* **1997**, *36*, 5424–5425.
- (63) Ogo, S.; Wada, S.; Watanabe, Y.; Iwase, M.; Wada, A.; Harata, M.; Jitsukawa, K.; Masuda, H.; Einaga, H. *Angew. Chem. Int. Ed.* **1998**, *37*, 2102–2104.
- (64) Kim, J.; Zang, Y.; Costas, M.; Harrison, R. G.; Wilkinson, E. C.; Que Jr, L. *J. Biol. Inorg. Chem.* **2001**, *6*, 275–284.
- (65) Jonas, R. T.; Stack, T. *J. Am. Chem. Soc.* **1997**, *119*, 8566–8567.
- (66) Goldsmith, C. R.; Jonas, R. T.; Stack, T. D. P. *J. Am. Chem. Soc.* **2002**, *124*, 83–96.
- (67) Nelson, M. J. *Biochemistry* **1988**, *27*, 4273–4278.
- (68) Goldsmith, C. R.; Cole, A. P.; Stack, T. D. P. *J. Am. Chem. Soc.* **2005**, *127*, 9904–9912.
- (69) Goldsmith, C. R.; Stack, T. D. P. *Inorg. Chem.* **2006**, *45*, 6048–6055.
- (70) Ohzu, S.; Ishizuka, T.; Kotani, H.; Kojima, T. *Chem. Commun.* **2014**, *50*, 15018–15021.
- (71) Mei, F.; Ou, C.; Wu, G.; Cao, L.; Han, F.; Meng, X.; Li, J.; Li, D.; Liao, Z. *Dalton Trans.* **2010**, *39*, 4267–4269.
- (72) Wu, G.; Mei, F.; Gao, Q.; Han, F.; Lan, S.; Zhang, J.; Li, D. *Dalton Trans.* **2011**, *40*, 6433–6439.
- (73) Porter, T. R.; Mayer, J. M. *Chem. Sci.* **2014**, *5*, 372–380.
- (74) Gao, H.; Groves, J. T. *J. Am. Chem. Soc.* **2017**, *139*, 3938–3941.
- (75) Wijeratne, G. B.; Corzine, B.; Day, V. W.; Jackson, T. A. *Inorg. Chem.* **2014**, *53*, 7622–7634.
- (76) Wijeratne, G. B.; Day, V. W.; Jackson, T. A. *Dalton Trans.* **2015**, *44*, 3295–3306.
- (77) Rice, D. B.; Wijeratne, G. B.; Burr, A. D.; Parham, J. D.; Day, V. W.; Jackson, T. A. *Inorg. Chem.* **2016**, *55*, 8110–8120.
- (78) Coggins, M. K.; Brines, L. M.; Kovacs, J. A. *Inorg. Chem.* **2013**, *52*, 12383–12393.
- (79) Brines, L. M.; Coggins, M. K.; Poon, P. C. Y.; Toledo, S.; Kaminsky, W.; Kirk, M. L.; Kovacs, J. A. *J. Am. Chem. Soc.* **2015**, *137*, 2253–2264.
- (80) Kurahashi, T.; Kikuchi, A.; Tosha, T.; Shiro, Y.; Kitagawa, T.; Fujii, H. *Inorg. Chem.* **2008**, *47*, 1674–1686.
- (81) Kurahashi, T.; Kikuchi, A.; Shiro, Y.; Hada, M.; Fujii, H. *Inorg. Chem.* **2010**, *49*, 6664–6672.

- (82) Yin, G.; McCormick, J. M.; Buchalova, M.; Danby, A. M.; Rodgers, K.; Day, V. W.; Smith, K.; Perkins, C. M.; Kitko, D.; Carter, J. D. *Inorg. Chem.* **2006**, *45*, 8052–8061.
- (83) Yin, G.; Danby, A. M.; Kitko, D.; Carter, J. D.; Scheper, W. M.; Busch, D. H. *J. Am. Chem. Soc.* **2007**, *129*, 1512–1513.
- (84) Yin, G.; Danby, A. M.; Kitko, D.; Carter, J. D.; Scheper, W. M.; Busch, D. H. *J. Am. Chem. Soc.* **2008**, *130*, 16245–16253.
- (85) Chattopadhyay, S.; Geiger, R. A.; Yin, G.; Busch, D. H.; Jackson, T. A. *Inorg. Chem.* **2010**, *49*, 7530–7535.
- (86) Shi, S.; Wang, Y.; Xu, A.; Wang, H.; Zhu, D.; Roy, S. B.; Jackson, T. A.; Busch, D. H.; Yin, G. *Angew. Chem. Int. Ed.* **2011**, *50*, 7321–7324.
- (87) Yin, G. *Acc. Chem. Res.* **2013**, *46*, 483–492.
- (88) Xu, A.; Xiong, H.; Yin, G. *Chem. Eur. J.* **2009**, *15*, 11478–11481.
- (89) Yin, G. *Coord. Chem. Rev.* **2010**, *254*, 1826–1842.
- (90) Wang, Y.; Shi, S.; Wang, H.; Zhu, D.; Yin, G. *Chem. Commun.* **2012**, *48*, 7832–7834.
- (91) Fiedler, A. T.; Que Jr, L. *Inorg. Chem.* **2009**, *48*, 11038–11047.
- (92) Shirin, Z.; Hammes, B. S.; Young, V. G.; Borovik, A. *J. Am. Chem. Soc.* **2000**, *122*, 1836–1837.
- (93) Gupta, R.; MacBeth, C. E.; Young, V. G.; Borovik, A. *J. Am. Chem. Soc.* **2002**, *124*, 1136–1137.
- (94) Gupta, R.; Borovik, A. *J. Am. Chem. Soc.* **2003**, *125*, 13234–13242.
- (95) MacBeth, C. E.; Gupta, R.; Mitchell-Koch, K. R.; Young, V. G.; Lushington, G. H.; Thompson, W. H.; Hendrich, M. P.; Borovik, A. *J. Am. Chem. Soc.* **2004**, *126*, 2556–2567.
- (96) Parsell, T. H.; Behan, R. K.; Green, M. T.; Hendrich, M. P.; Borovik, A. *J. Am. Chem. Soc.* **2006**, *128*, 8728–8729.
- (97) Parsell, T. H.; Yang, M.-Y.; Borovik, A. *J. Am. Chem. Soc.* **2009**, *131*, 2762–2763.
- (98) Taguchi, T.; Gupta, R.; Lassalle-Kaiser, B.; Boyce, D. W.; Yachandra, V. K.; Tolman, W. B.; Yano, J.; Hendrich, M. P.; Borovik, A. *J. Am. Chem. Soc.* **2012**, *134*, 1996–1999.
- (99) Gupta, R.; Taguchi, T.; Borovik, A.; Hendrich, M. P. *Inorg. Chem.* **2013**, *52*, 12568–12575.
- (100) Taguchi, T.; Stone, K. L.; Gupta, R.; Kaiser-Lassalle, B.; Yano, J.; Hendrich, M. P.; Borovik, A. *Chem. Sci.* **2014**, *5*, 3064–3071.
- (101) Shook, R. L.; Peterson, S. M.; Greaves, J.; Moore, C.; Rheingold, A. L.; Borovik, A. *J. Am. Chem. Soc.* **2011**, *133*, 5810–5817.
- (102) MacBeth, C. E.; Golombek, A. P.; Young, V. G.; Yang, C.; Kuczera, K.; Hendrich, M. P.; Borovik, A. *Science* **2000**, *289*, 938–941.
- (103) Lacy, D. C.; Gupta, R.; Stone, K. L.; Greaves, J.; Ziller, J. W.; Hendrich, M. P.; Borovik, A. *J. Am. Chem. Soc.* **2010**, *132*, 12188–12190.
- (104) Hill, E. A.; Weitz, A. C.; Onderko, E.; Romero-Rivera, A.; Guo, Y.; Swart, M.; Bominaar, E. L.; Green, M. T.; Hendrich, M. P.; Lacy, D. C. *J. Am. Chem. Soc.* **2016**, *138*, 13143–13146.
- (105) Park, Y. J.; Matson, E. M.; Nilges, M. J.; Fout, A. R. *Chem. Commun.* **2015**, *51*, 5310–5313.
- (106) Matson, E. M.; Bertke, J. A.; Fout, A. R. *Inorg. Chem.* **2014**, *53*, 4450–4458.
- (107) Gordon, Z.; Drummond, M. J.; Matson, E. M.; Bogart, J. A.; Schelter, E. J.; Lord, R. L.; Fout, A. R. *Inorg. Chem.* **2017**, *56*, 4852–863.
- (108) Matson, E. M.; Park, Y. J.; Fout, A. R. *J. Am. Chem. Soc.* **2014**, *136*, 17398–17401.
- (109) Ford, C. L.; Park, Y. J.; Matson, E. M.; Gordon, Z.; Fout, A. R. *Science* **2016**, *354*, 741–743.
- (110) Lau, T.-C.; Wu, Z.-B.; Bai, Z.-L.; Mak, C.-K. *J. Chem. Soc., Dalton Trans.* **1995**, 695–696.
- (111) Lam, W. W. Y.; Yiu, S.-M.; Lee, J. M. N.; Yau, S. K. Y.; Kwong, H.-K.; Lau, T.-C.; Liu, D.; Lin, Z. *J. Am. Chem. Soc.* **2006**, *128*, 2851–2858.
- (112) Du, H.; Lo, P.-K.; Hu, Z.; Liang, H.; Lau, K.-C.; Wang, Y.-N.; Lam, W. W. Y.; Lau, T.-C. *Chem. Commun.* **2011**, *47*, 7143–7145.
- (113) Ho, C.-M.; Lau, T.-C. *New J. Chem.* **2000**, *24*, 587–590.
- (114) Lau, T.-C.; Mak, C.-K. *J. Chem. Soc., Chem. Commun.* **1993**, 766–767.
- (115) Miller, C. G.; Gordon-Wylie, S. W.; Horwitz, C. P.; Strazisar, S. A.; Peraino, D. K.; Clark, G. R.; Weintraub, S. T.; Collins, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 11540–11541.
- (116) Chen, J.; Lee, Y.-M.; Davis, K. M.; Wu, X.; Seo, M. S.; Cho, K.-B.; Yoon, H.; Park, Y. J.; Fukuzumi, S.; Pushkar, Y. N. *J. Am. Chem. Soc.* **2013**, *135*, 6388–6391.

- (117) Yoon, H.; Lee, Y.-M.; Wu, X.; Cho, K.-B.; Sarangi, R.; Nam, W.; Fukuzumi, S. *J. Am. Chem. Soc.* **2013**, *135*, 9186–9194.
- (118) Dong, L.; Wang, Y.; Lv, Y.; Chen, Z.; Mei, F.; Xiong, H.; Yin, G. *Inorg. Chem.* **2013**, *52*, 5418–5427.
- (119) Leeladee, P.; Baglia, R. A.; Prokop, K. A.; Latifi, R.; de Visser, S. P.; Goldberg, D. P. *J. Am. Chem. Soc.* **2012**, *134*, 10397–10400.
- (120) Baglia, R. A.; Dürr, M.; Ivanović-Burmazović, I.; Goldberg, D. P. *Inorg. Chem.* **2014**, *53*, 5893–5895.
- (121) Baglia, R. A.; Krest, C. M.; Yang, T.; Leeladee, P.; Goldberg, D. P. *Inorg. Chem.* **2016**, *55*, 10800–10809.
- (122) Zaragoza, J. P. T.; Baglia, R. A.; Siegler, M. A.; Goldberg, D. P. *J. Am. Chem. Soc.* **2015**, *137*, 6531–6540.
- (123) Bougher, C. J.; Liu, S.; Hicks, S. D.; Abu-Omar, M. M. *J. Am. Chem. Soc.* **2015**, *137*, 14481–14487.
- (124) Fukuzumi, S.; Morimoto, Y.; Kotani, H.; Naumov, P.; Lee, Y.-M.; Nam, W. *Nat. Chem.* **2010**, *2*, 756–759.
- (125) Swart, M. *Chem. Commun.* **2013**, *49*, 6650–6652.
- (126) Prakash, J.; Rohde, G. T.; Meier, K. K.; Jasniowski, A. J.; Van Heuvelen, K. M.; Münck, E.; Que, L. *J. Am. Chem. Soc.* **2015**, *137*, 3478–3481.
- (127) Morimoto, Y.; Kotani, H.; Park, J.; Lee, Y.-M.; Nam, W.; Fukuzumi, S. *J. Am. Chem. Soc.* **2011**, *133*, 403–405.
- (128) Morimoto, Y.; Park, J.; Suenobu, T.; Lee, Y.-M.; Nam, W.; Fukuzumi, S. *Inorg. Chem.* **2012**, *51*, 10025–10036.
- (129) Park, J.; Morimoto, Y.; Lee, Y.-M.; Nam, W.; Fukuzumi, S. *J. Am. Chem. Soc.* **2012**, *134*, 3903–3911.
- (130) Park, J.; Morimoto, Y.; Lee, Y.-M.; Nam, W.; Fukuzumi, S. *Inorg. Chem.* **2014**, *53*, 3618–3628.
- (131) Park, J.; Morimoto, Y.; Lee, Y.-M.; Nam, W.; Fukuzumi, S. *J. Am. Chem. Soc.* **2011**, *133*, 5236–5239.
- (132) Park, J.; Morimoto, Y.; Lee, Y.-M.; You, Y.; Nam, W.; Fukuzumi, S. *Inorg. Chem.* **2011**, *50*, 11612–11622.
- (133) Park, Y. J.; Cook, S. A.; Sickerman, N. S.; Sano, Y.; Ziller, J. W.; Borovik, A. *Chem. Sci.* **2013**, *4*, 717–726.
- (134) Lacy, D. C.; Park, Y. J.; Ziller, J. W.; Yano, J.; Borovik, A. *J. Am. Chem. Soc.* **2012**, *134*, 17526–17535.
- (135) Pfaff, F. F.; Kundu, S.; Risch, M.; Pandian, S.; Heims, F.; Pryjomska-Ray, I.; Haack, P.; Metzinger, R.; Bill, E.; Dau, H. *Angew. Chem. Int. Ed.* **2011**, *50*, 1711–1715.
- (136) Hong, S.; Pfaff, F. F.; Kwon, E.; Wang, Y.; Seo, M.; Bill, E.; Ray, K.; Nam, W. *Angew. Chem. Int. Ed.* **2014**, *53*, 10403–10407.
- (137) Pfaff, F. F.; Heims, F.; Kundu, S.; Mebs, S.; Ray, K. *Chem. Commun.* **2012**, *48*, 3730–3732.
- (138) Donoghue, P. J.; Tehranchi, J.; Cramer, C. J.; Sarangi, R.; Solomon, E. I.; Tolman, W. B. *J. Am. Chem. Soc.* **2011**, *133*, 17602–17605.
- (139) Dhar, D.; Tolman, W. B. *J. Am. Chem. Soc.* **2015**, *137*, 1322–1329.
- (140) Halvagar, M. R.; Tolman, W. B. *Inorg. Chem.* **2013**, *52*, 8306–8308.
- (141) Dhar, D.; Yee, G. M.; Spaeth, A. D.; Boyce, D. W.; Zhang, H.; Dereli, B.; Cramer, C. J.; Tolman, W. B. *J. Am. Chem. Soc.* **2016**, *138*, 356–368.
- (142) Gagnon, N.; Tolman, W. B. *Acc. Chem. Res.* **2015**, *48*, 2126–2131.
- (143) Dhar, D.; Yee, G. M.; Markle, T. F.; Mayer, J. M.; Tolman, W. B. *Chem. Sci.* **2017**, *8*, 1075–1085.
- (144) Thomas, F. *Eur. J. Inorg. Chem.* **2007**, *2007*, 2379–2404.
- (145) Lyons, C. T.; Stack, T. D. P. *Coord. Chem. Rev.* **2013**, *257*, 528–540.
- (146) Philibert, A.; Thomas, F.; Philouze, C.; Hamman, S.; Saint-Aman, E.; Pierre, J.-L. *Chem. Eur. J.* **2003**, *9*, 3803–3812.
- (147) Goldsmith, C. R.; Jonas, R. T.; Stack, T. D. P. *J. Am. Chem. Soc.* **2002**, *124*, 83–96.
- (148) Neu, H. M.; Yang, T.; Baglia, R. A.; Yosca, T. H.; Green, M. T.; Quesne, M. G.; de Visser, S. P.; Goldberg, D. P. *J. Am. Chem. Soc.* **2014**, *136*, 13845–13852.
- (149) Green, M. T. *Curr. Opin. Chem. Biol.* **2009**, *13*, 84–88.

- (150) Li, X.-X.; Postils, V.; Sun, W.; Faponle, A. S.; Solà, M.; Wang, Y.; Nam, W.; de Visser, S. P. *Chem. Eur. J.* **2017**, *23*, 6406–6418.
- (151) Westheimer, F. H. *Chem. Rev.* **1961**, *61*, 265–273.
- (152) Kwart, H. *Acc. Chem. Res.* **1982**, *15*, 401–408.
- (153) Li, Y.; Zamble, D. B. *Chem. Rev.* **2009**, *109*, 4617–4643.
- (154) Dai, Y.; Wensink, P. C.; Abeles, R. H.; Robert, H. J. *Biol. Chem.* **1999**, *274*, 1193–1195.
- (155) Jeoung, J.-H.; Nianios, D.; Fetzner, S.; Dobbek, H. *Angew. Chem. Int. Ed.* **2016**, *55*, 3281–3284.
- (156) Maroney, M. J.; Ciurli, S. *Chem. Rev.* **2014**, *114*, 4206–4228.
- (157) Yoon, H.; Wagler, T. R.; O'Connor, K. J.; Burrows, C. J. *J. Am. Chem. Soc.* **1990**, *112*, 4568–4570.
- (158) Irie, R.; Ito, Y.; Katsuki, T. *Tetrahedron Lett.* **1991**, *32*, 6891–6894.
- (159) Yamada, T.; Takai, T.; Rhode, O.; Mukaiyama, T. *Chem. Lett.* **1991**, *20*, 1–4.
- (160) Fernández, I.; Pedro, J. R.; Roselló, A. L.; Ruiz, R.; Ottenwaelder, X.; Journaux, Y. *Tetrahedron Lett.* **1998**, *39*, 2869–2872.
- (161) Koola, J. D.; Kochi, J. K. *Inorg. Chem.* **1987**, *26*, 908–916.
- (162) Kinneary, J. F.; Albert, J. S.; Burrows, C. J. *J. Am. Chem. Soc.* **1988**, *110*, 6124–6129.
- (163) Solans-Monfort, X.; Fierro, J. L. G.; Hermosilla, L.; Sieiro, C.; Sodupe, M.; Mas-Ballesté, R. *Dalton Trans.* **2011**, *40*, 6868–6876.
- (164) Nagataki, T.; Tachi, Y.; Itoh, S. *Chem. Commun.* **2006**, *14*, 4016–4018.
- (165) Nagataki, T.; Ishii, K.; Tachi, Y.; Itoh, S. *Dalton Trans.* **2007**, *21*, 1120–1128.
- (166) Nagataki, T.; Itoh, S. *Chem. Lett.* **2007**, *36*, 748–749.
- (167) Balamurugan, M.; Mayilmurugan, R.; Suresh, E.; Palaniandavar, M. *Dalton Trans.* **2011**, *40*, 9413–9424.
- (168) Sankaralingam, M.; Vadivelu, P.; Suresh, E.; Palaniandavar, M. *Inorg. Chim. Acta* **2013**, *407*, 98–107.
- (169) Sankaralingam, M.; Balamurugan, M.; Palaniandavar, M.; Vadivelu, P.; Suresh, C. H. *Chem. Eur. J.* **2014**, *20*, 11346–11361.
- (170) Hikichi, S.; Hanaue, K.; Fujimura, T.; Okuda, H.; Nakazawa, J.; Ohzu, Y.; Kobayashi, C.; Akita, M. *Dalton Trans.* **2013**, *42*, 3346–3356.
- (171) Morimoto, Y.; Bunno, S.; Fujieda, N.; Sugimoto, H.; Itoh, S. *J. Am. Chem. Soc.* **2015**, *137*, 5867–5870.
- (172) 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*, 13043–13049.
- (173) Zhang, M.; Zhang, M.-T.; Hou, C.; Ke, Z.-F.; Lu, T.-B. *Angew. Chem. Int. Ed.* **2014**, *53*, 13042–13048.
- (174) Draksharapu, A.; Codolá, Z.; Gómez, L.; Lloret-Fillol, J.; Browne, W. R.; Costas, M. *Inorg. Chem.* **2015**, *54*, 10656–10666.
- (175) Corona, T.; Company, A. *Chem. Eur. J.* **2016**, *22*, 13422–13429.
- (176) Hikichi, S.; Yoshizawa, M.; Sasakura, Y.; Akita, M.; Moro-oka, Y. *J. Am. Chem. Soc.* **1998**, *120*, 10567–10568.
- (177) Itoh, S.; Bandoh, H.; Nagatomo, S.; Kitagawa, T.; Fukuzumi, S. *J. Am. Chem. Soc.* **1999**, *121*, 8945–8946.
- (178) Shiren, K.; Ogo, S.; Fujinami, S.; Hayashi, H.; Suzuki, M.; Uehara, A.; Watanabe, Y.; Moro-oka, Y. *J. Am. Chem. Soc.* **2000**, *122*, 254–262.
- (179) Itoh, S.; Bandoh, H.; Nakagawa, M.; Nagatomo, S.; Kitagawa, T.; Karlin, K. D.; Fukuzumi, S. *J. Am. Chem. Soc.* **2001**, *123*, 11168–11178.
- (180) Schenker, R.; Mandimutsira, B. S.; Riordan, C. G.; Brunold, T. C. *J. Am. Chem. Soc.* **2002**, *124*, 13842–13855.
- (181) Fujita, K.; Schenker, R.; Gu, W.; Brunold, T. C.; Cramer, S. P.; Riordan, C. G. *Inorg. Chem.* **2004**, *43*, 3324–3326.
- (182) Corona, T.; Draksharapu, A.; Padamati, S. K.; Gamba, I.; Martin-Diaconescu, V.; Acuña-Parés, F.; Browne, W. R.; Company, A. *J. Am. Chem. Soc.* **2016**, *138*, 12987–12996.
- (183) Chmielewski, P. J.; Latos-Grażyński, L. *Inorg. Chem.* **1997**, *36*, 840–845.
- (184) Chiou, T.-W.; Liaw, W.-F. *Inorg. Chem.* **2008**, *47*, 7908–7913.
- (185) Zhou, W.; Schultz, J. W.; Rath, N. P.; Mirica, L. M. *J. Am. Chem. Soc.* **2015**, *137*, 7604–7607.

- (186) Collins, T. J. *Acc Chem Res* **2002**, 35, 782–790.
- (187) Van Koten, G. J. *J. Organomet. Chem.* **2013**, 730, 156–164.
- (188) Deng, Q.-H.; Melen, R. L.; Gade, L. H. *Acc. Chem. Res.* **2014**, 47, 3162–3173.
- (189) Donoghue, P. J.; Gupta, A. K.; Boyce, D. W.; Cramer, C. J.; Tolman, W. B. *J. Am. Chem. Soc.* **2010**, 132, 15869–15871.
- (190) Patra, A. K.; Mukherjee, R. *Inorg. Chem.* **1999**, 38, 1388–1393.

Chapter 2

Characterisation and Oxidising Reactivity of a Nickel(III) Bicarbonate Complex

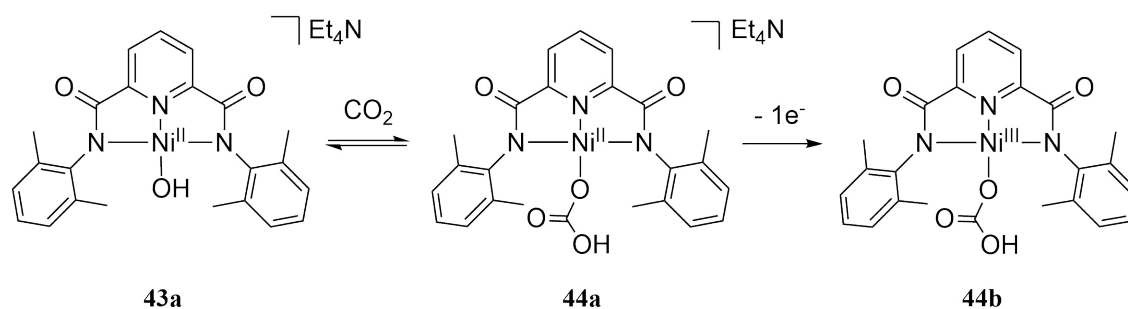
The work described in this chapter has been previously published in an article in Chemistry – A European Journal.¹ The DFT calculations were performed by Prof. Marcel Swart (University of Girona, Spain); the XAS data collection and analysis were done by Dr Eric R. Farquhar (Brookhaven National Laboratory, USA); Dr. A.J. Fitzpatrick and Prof. Grace G. Morgan (University College Dublin) kindly allowed use of the EPR spectrometer and helped with spectra acquisition.

Reproduced in part with permission from: Pirovano, P.; Farquhar, E. R.; Swart, M.; Fitzpatrick, A. J.; Morgan, G. G.; McDonald, A. R. *Chem. Eur. J.* **2015**, 21, 3785–3790. Copyright 2015 John Wiley and Sons.

2.1 Introduction

As outlined in sections 1.5 and 1.6, the small number of well-characterised, high valent nickel complexes in the literature poses an obstacle to the investigation of their oxidative reactivity. At the start of this work, the few known mononuclear, terminal $\text{Ni}^{\text{III}}\text{--O--X}$ species had either limited characterisation, or were not known to react with oxidisable substrates.^{2–5}

Holm has reported the synthesis of a series of $[\text{Ni}^{\text{II}}(\text{OH})(\text{pyN}_2^{\text{R}_2})]^-$ complexes, and demonstrated the reactivity of the hydroxo ligand as a base or nucleophile.^{6–9} One important result was the observation that, on exposure to atmospheric CO_2 , $[\text{Ni}^{\text{II}}(\text{OH})(\text{pyN}_2^{\text{Me}_2})]^-$ (**43**) reacted to form a terminal bicarbonato complex, $[\text{Ni}^{\text{II}}(\text{OCO}_2\text{H})(\text{pyN}_2^{\text{Me}_2})]^-$, **44a** (sch. 2.1). These compounds were selected as starting materials for the preparation of high-valent Ni--O--X oxidants. While attempts at the oxidation of the $\text{Ni}^{\text{II}}\text{--OH}$ complex did not prove fruitful, I describe in this chapter the successful oxidation of **44a**, to yield a metastable $\text{Ni}^{\text{III}}\text{--O--X}$ species that is capable of oxidising organic substrates.



Scheme 2.1. Complexes $[\text{Ni}^{\text{II}}(\text{OH})(\text{pyN}_2^{\text{Me}_2})]$, **44a**, and **44b**. Schematic representation of the preparation of **44a** and **44b**.

2.2 Formation and characterisation of a nickel(III) bicarbonato complex

In acetone, at $-80\text{ }^\circ\text{C}$, **44a** was reacted with the organic oxidant tris(4-bromophenyl)-ammoniumyl hexachloroantimonate¹⁰ ('magic blue', dissolved in CH_3CN , $E^\circ = 0.70\text{ V}$ vs $\text{Fc}^+/\text{Fc}^{11}$). An instantaneous reaction was observed as evidenced by the appearance of two intense features in the electronic absorption spectrum ($\lambda_{\text{max}} = 520$ and 790 nm , fig. 2.1a), assigned to a novel species **44b**. A titration of magic blue against **44a** showed that the

intensity of the new features reached a maximum after the addition of one equivalent of magic blue (fig. 2.1a, inset). The addition of greater than one equivalent of magic blue did not cause a further change in the new features, while the presence of excess unreacted magic blue in the reaction mixture was observed in the electronic absorption spectrum (fig. 2.1b). Initial indications thus suggested that **44a** had been oxidized by one electron yielding a novel species, **44b**, postulated to be a $\text{Ni}^{\text{III}}\text{-OCO}_2\text{H}$ complex.

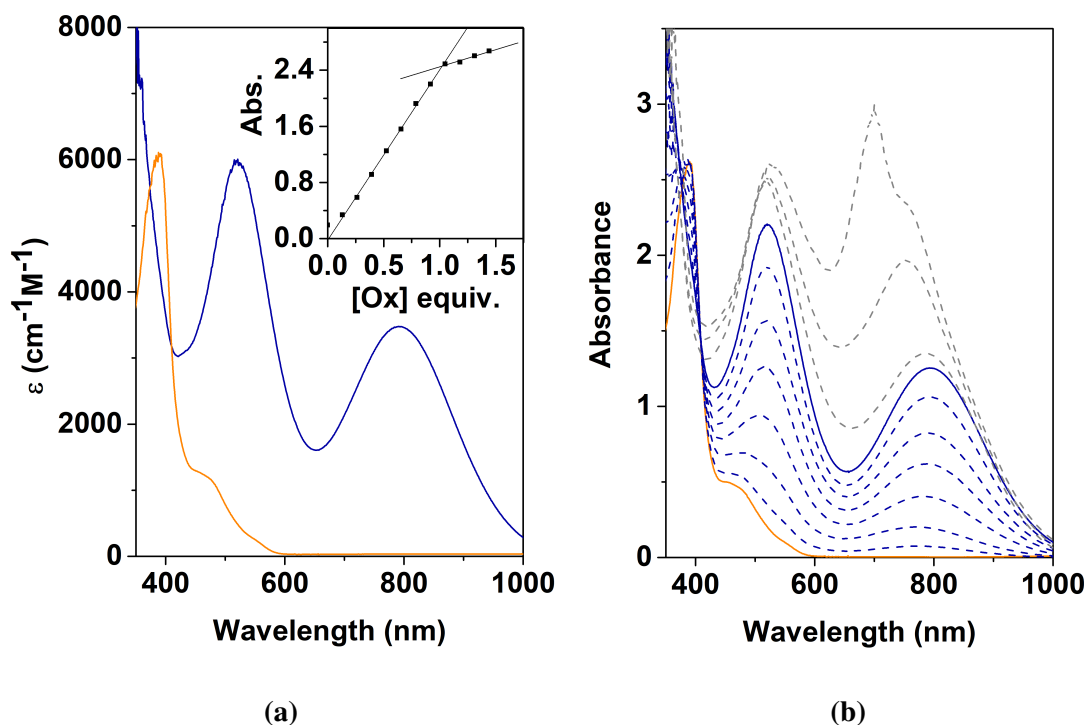


Figure 2.1. (a) UV-Vis spectrum of **44a** (orange trace, 0.4 mM in acetone) that was reacted with magic blue at -80°C to yield **44b** (blue trace). Inset: Titration of **44a** with magic blue monitored by plotting the intensity of the $\lambda_{\text{max}} = 520\text{ nm}$ feature versus equivalents of magic blue. (b) UV-Vis spectral changes during the titration of **44a** (0.4 mM, acetone solution, solid orange trace) with 15 mM magic blue solution in acetonitrile at -80°C . The solid blue trace corresponds to the addition of 1 equivalent of oxidant, and the dashed grey traces to further addition of excess oxidant.

The intense absorption features in the visible and near-IR (NIR) regions of the UV-Vis spectrum, observed upon the reaction between **44a** and magic blue to yield **44b**, suggest a change in the oxidation state of the Ni centre. Many of the Ni^{III} complexes reported to date display similarly intense chromophores in the visible and NIR regions of their absorption spectra.^{3,5,12–19} Intermediate **44b** could be generated in acetone or THF. The features associated with **44b** are the same in both solvents. Likewise, when **44b** was prepared in the presence or absence of excess CH_3CN (acetone or CH_3CN can be used as the solvent for

magic blue) no difference in the electronic absorption features was noted. These observations are important as they demonstrate that solvent is not coordinating to the Ni^{III} centre in **44b**. Should solvent coordinate to the Ni^{III} centre in **44b**, one would anticipate different UV-Vis characteristics of the oxidized product in different solvent media.

2.2.1 EPR spectroscopy

44b was further characterized using X-band electron paramagnetic resonance (EPR) spectroscopy. An acetone solution of **44b** was frozen in liquid nitrogen and an axial spectrum was obtained at 113 K (fig. 2.2, $g_{\perp} = 2.25$, $g_{\parallel} = 2.02$). The yield of Ni^{III} was calculated to be 95% ($\pm 15\%$) by double integration of the signal of **44b** against that of a radical standard (TEMPO). The obtained g -values are consistent with an $S = \frac{1}{2}$ (low-spin) d^7 Ni^{III} species,^{16,20–22} and the average g -value ($g_{\text{av.}} = 2.17$) is indicative of the unpaired electron sitting on the Ni centre, rather than being a ligand-based radical. Importantly, $g_{\perp} > g_{\parallel}$, which is typical for axially elongated octahedral complexes or square planar complexes.^{14,16,20–26}

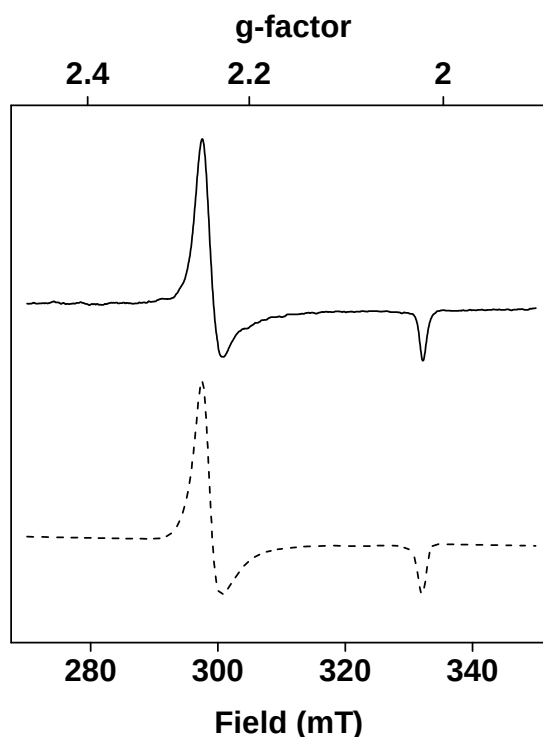


Figure 2.2. Solid trace: X-band EPR spectrum of **44b** in a frozen acetone solution. Measured at 113 K; microwave power = 31.6 mW; modulation amplitude = 0.5 mT; $g_{\perp} = 2.25$, $g_{\parallel} = 2.02$, $g_{\text{av.}} = 2.17$. Dashed trace: simulated spectrum for **44b**. The system was modelled as an $S = \frac{1}{2}$ electron spin with axial g tensor, and inhomogeneous line broadening. The greater line broadening in the x and y directions is possibly due to unresolved hyperfine coupling with the ^{14}N nuclei of the ligand.

The most likely configurations for a low-spin d^7 ion in pseudo-tetragonal symmetry involve the unpaired electron density being located in an orbital of predominant d_{z^2} or d_{xy} character. Instances where $g_{\perp} > g_{\parallel}$ have been usually understood to correspond to a d_{z^2} singly-occupied orbital.^{14,16,20–22,24,26} In all, the EPR analysis suggests that oxidation of the square-planar precursor **44a** resulted in the loss of an electron yielding a square-planar, $S = 1/2$, d^7 , Ni^{III} species, **44b**, with a metal-based d_{z^2} -like occupied orbital.

Density functional theory (DFT) Mulliken spin density calculations were performed in order to further probe the location of the unpaired electron density in **44b**. These calculations supported the experimental observations that the unpaired spin predominantly resides in a metal-based molecular orbital. The DFT calculations predict that either metal-based d_{z^2} - or d_{xy} -like molecular orbitals are the likely locations of the unpaired electron density (fig. 2.3 displays spin density plot for d_{z^2} occupancy). The DFT calculations thus support the EPR determined electronic structure of **44b**.

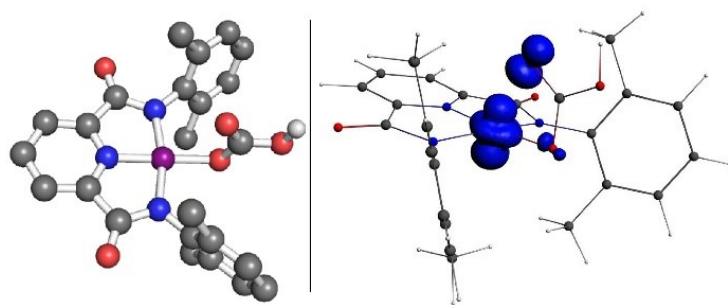


Figure 2.3. Left: DFT optimized structure of **44b**. Hydrogen atoms (except bicarbonate proton) have been excluded for clarity. Right: DFT optimized spin density plot of **44b**.

Table 2.1. Nickel-ligand bond distances for **44a** and **44b** as determined using: [a] XRD; [b] EX-AFS; and [c] DFT.

	Ni–OCO ₂ H	Ni–N _{pyridine}	Ni–N _{amido}
44a ^[a] ⁶	1.871(4)	1.817(4)	2 at 1.895(4)
44a ^[b]		4 at 1.87	
44a ^[c]	1.90	1.80	2 at 1.90
44b ^[b]	2 at 1.84		2 at 1.99
44b ^[c]	1.96	1.84	2 at 1.93

2.2.2 X-Ray absorption spectroscopy

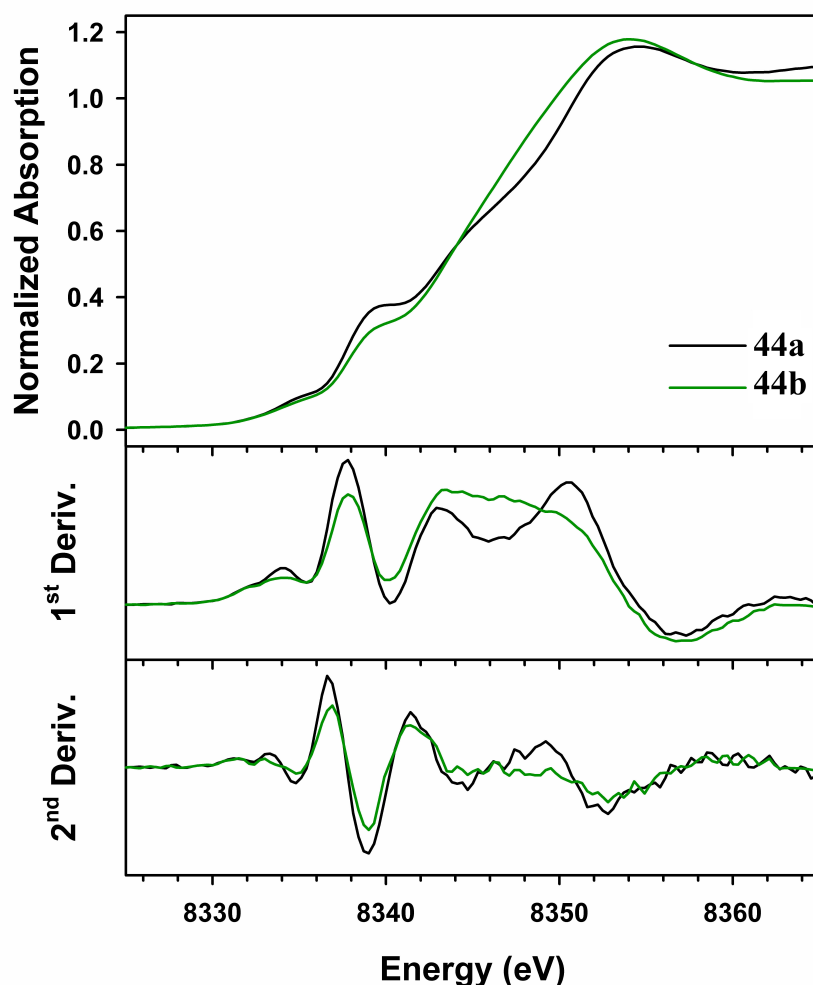


Figure 2.4. XANES spectra of **44a** (black trace) and **44b** (green trace), along with associated first and second derivatives.

X-ray absorption spectroscopy (XAS) was employed to analyse the electronic and structural properties of **44b**. The XAS K edge energy measured for **44b** (8345 eV) lies in the expected range for Ni^{III} complexes.^{27–29} Interestingly, there is only a very minor shift in the K-edge energy compared to the K-edge energy measured for Ni^{II} -containing **44a** (fig. 2.4). This is not unusual for Ni (and indeed Cu) K-edge analysis, several groups have made similar observations when comparing $\text{Ni}^{\text{II/III}}$ species within comparable coordination environments.^{28,30–32} Contributions to the edge from $1s \rightarrow 4p$ absorption features distort

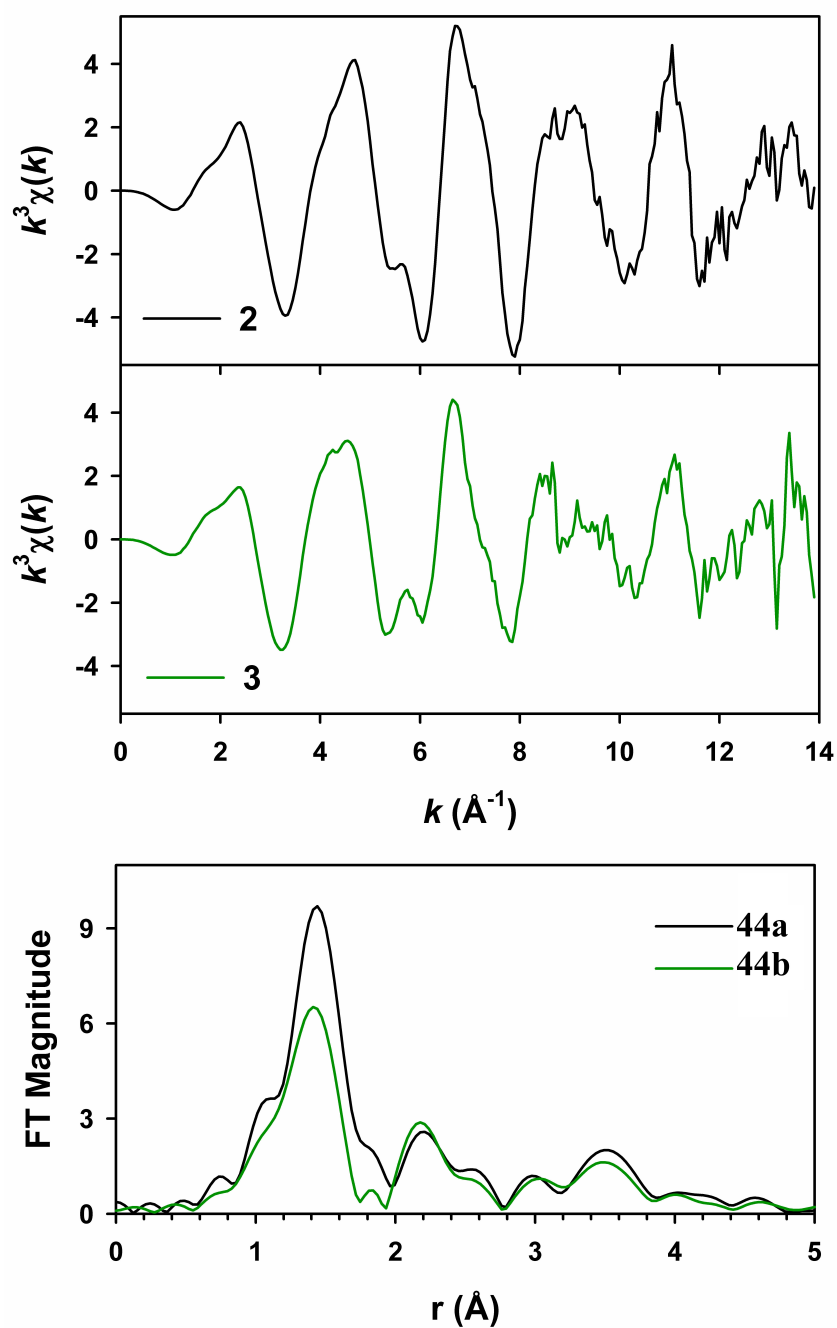


Figure 2.5. (top) $k^3\chi(k)$ EXAFS spectra of **44a** (black trace) and **44b** (green trace). (bottom) Fourier transforms of the $k^3\chi(k)$ EXAFS ($k = 1.5\text{--}13.5$ $\text{\AA}^{-1}$ for **44a**, $k = 1.5\text{--}13$ $\text{\AA}^{-1}$ for **44b**).

the edge and prevent accurate assessment of the edge shift upon oxidation of **44a** to yield **44b**.

The derivatives of the normalized X-ray absorption near-edge spectrum (XANES) indicate a modest edge shift of 0.1 - 0.2 eV when comparing the $1s \rightarrow 3d$ pre-edge transition of **44a** to **44b**, in accord with increased oxidation of the Ni centre in **44b**. Although there appears to be negligible change in the edge energy between **44a** and **44b**, the shape of the edge and relative intensities of features in the edge are markedly different. Such differences are indicative of the distinct electronic environments of the Ni-centre in complexes **44a** and **44b**.

Extended X-ray absorption fine structure (EXAFS) analysis of **44b** yielded a disordered first coordination shell of 4 O/N donors (fig. 2.5, table 2.2 in the experimental section). This shell could be split into two components with two scatterers at ~ 1.84 Å and two scatterers at ~ 1.99 Å giving the best fit of the experimental data obtained for **44b** (table 2.1). These observations suggest that a single-bonded oxygen ligand is present in **44b**, *i.e.* the bicarbonate remains intact. Fits with 5 N/O donors were also reasonably good, and the EXAFS analysis cannot conclusively exclude this possibility. Attempts to fit the data containing a very short Ni–O bond (~ 1.65 Å) resulted in very poor fits, ruling out the possibility of **44b** being a $\text{Ni}^{\text{III}}=\text{O}$ species. Comparison of the EXAFS fits for **44a** and **44b** suggests there are little to no structural differences in the two complexes. The fits acquired for **44a** match well with the X-ray diffraction determined bond distances obtained for **44a**.⁶

2.2.3 DFT calculations

DFT was employed to further understand the structural properties of **44b** (table 2.1, fig. 2.3). The DFT predictions indicate that the bicarbonate ligand in **44b** would remain bound in a monodentate fashion, in good agreement with the EXAFS analyses of a first coordination sphere of 4 donors. Furthermore, the computational analyses predicted that the d^7 Ni^{III} ion in **44b** would remain in a square planar coordination environment analogous to that seen for **44b**, in good agreement with the EPR measurements that indicate the Ni^{III} ion sits in a square planar environ. DFT also predicted that the Ni–OCO₂H and Ni–N(py) bond distances in **44b** would be 1.96 Å and 1.84 Å (table 2.1), respectively, in reasonably good agreement with the EXAFS analyses showing two O/N scatterers at ~ 1.84 Å.

The combination of EXAFS and DFT predictions shows that the Ni centre in **44b** has remained 4-coordinate, in a square planar environment, and that the bicarbonate ligand is present. It is important to note that the obtained EXAFS data could also be reasonably well

fit with a –OH ligand (in place of –OCO₂H). Holm et al demonstrated that **44a** reversibly binds CO₂, and it is reasonable to suggest the affinity of **44b** for CO₂ may be less than for **44a**.^{6,7,9}

It was also endeavoured to probe **44b** using Raman spectroscopy, but failed to identify peaks that confirmed the presence of either –OH or –OCO₂H ligands; the rich Raman spectrum of the acetone support medium constituted a hurdle. Efforts to obtain mass spectrometric evidence for the molecular formula of **44b** also failed, presumably as a result of the low thermal stability of **44b**. It is important to note that oxidation of [Ni^{II}(OH)(pyN₂^{Me₂})][–] with magic blue does not yield the same spectroscopic features attributed to **44b**, but in fact yields as yet unidentified species. To conclude, **44b** is likely to maintain the coordinated –OCO₂H ligand.

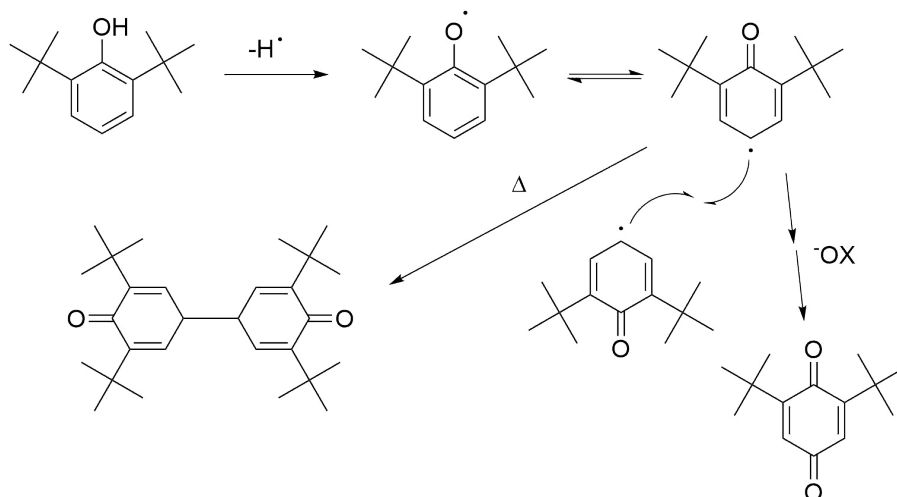
2.3 Oxidative reactivity

2.3.1 Oxidation of O–H bonds

44b was stable at –80 °C, but decayed upon warming above –40 °C. After warming to room temperature, the solution was EPR silent, indicating the disappearance of the oxidised species, suggesting the formation of as yet unidentified diamagnetic Ni^{II} species. After thermal decay and acidic work-up of the reaction mixture, the protonated ligand (H₂pyN₂^{Me₂}) was recovered without any indications of ligand oxidation (no evidence for ligand hydroxylation or oxidative decomposition was obtained by mass spectrometry or ¹H NMR spectroscopy).

The HAA reactivity of **44b** towards external substrates was investigated by reacting it with molecules containing weak O–H or C–H bonds. At –40 °C, **44b** reacted with 100 equiv. of 2,6-di-*tert*-butylphenol (2,6-DTBP), as evidenced by the disappearance over 600 s of the electronic absorption features attributed to **44b** (fig. A.1). This resulted in the appearance of a new band at $\lambda_{max} = 555$ nm, which can be attributed to the formation of the phenoxyl radical as a result of HAA from DTBP by **44b**.^{33,34} EPR analysis confirmed the formation of a phenoxyl radical (fig. A.2). After warming to room temperature, 3,3',5,5'-tetra-*tert*-butyl-[1,1'-bi(cyclohexane)]-2,2',5,5'-tetraene-4,4'-dione (sch. 2.2) and traces of 2,6-di-*tert*-butylquinone were detected using GC-MS. Such products form by radical coupling or thermal decomposition, respectively, of the parent 2,6-di-*tert*-butylphenoxyl radical.

A pseudo first-order rate constant (k_{obs}) for this reaction was determined by plotting the change in absorbance features for **44b** against time and fitting the resulting curve (fig. A.3).



Scheme 2.2. Formation of the final products from the oxidation of 2,6-DTBP by **44b**.

A second-order rate constant (k_2) was calculated from the slope of a linear plot of k_{obs} values determined under a series of substrate concentrations (fig. A.4). The k_2 value determined for the reaction between **44b** and 2,6-DTBP was $0.1040 \text{ M}^{-1} \text{ s}^{-1}$, while for deuterio-2,6-DTBP a k_2 value of $0.0503 \text{ M}^{-1} \text{ s}^{-1}$ was determined, yielding a KIE value of 2.1. This KIE value is consistent with **44b** performing HAT on the O–H bond of 2,6-DTBP, and with HAT being rate-limiting.

2.3.2 Oxidation of other substrates

44b was also found to react with 1-benzyl-1,4-dihydronicotinamide (BNAH, $\text{BDE}_{\text{C-H}} = 68 \text{ kcal/mol}$) at -80°C , as evidenced by a rapid disappearance of the visible absorption features attributed to **44b** (fig. A.5). The product of this reaction was identified by ^1H NMR spectroscopy as 1-benzyl-1-pyridinium-3-carboxamide, which typically forms as a result of HAT from the C–H bond of BNAH. This product formed as a result of a two-electron oxidation of BNAH. This likely occurs through initial HAT from BNAH followed by an electron transfer from the resultant product to another molecule of **44b**, although the oxidation could also proceed through a concerted hydride transfer step. In summary, **44b** was found to be a quite reactive HAT/PCET reagent capable of activating O–H and C–H bonds at low temperatures.

The capacity of **44b** to carry out OAT was also probed. **44b** was reacted with triphenylphosphine (PPh_3 , 50 equiv.) at -80°C resulting in the formation of triphenylphosphine oxide (PPh_3O , detected by ESI MS and ^{31}P NMR spectroscopy, fig. A.6). OAT is a two-electron transfer process, thus the formation of PPh_3O from this reaction would be expected to yield a Ni^{I} product. Such a Ni^{I} species was not observed, but rather only Ni^{II}

products. Presumably, the formed Ni^{I} product reacts with another molecule of **44b** (similar to the BNAH oxidation) to yield the observed Ni^{II} products; alternatively, the reaction proceeded through two successive one-electron transfer steps from two distinct **44b** molecules. **44b** was completely consumed by just 0.5 equivalents of PPh_3 and BNAH, confirming the suspicions about the mechanisms of its reductive decay.

A second-order rate constant (k_2) for the reaction between **44b** and PPh_3 was determined ($5.3 \text{ M}^{-1} \text{ s}^{-1}$, figs. A.7 and A.8). This k_2 value for PPh_3 oxidation is quite high compared to values determined for $\text{Fe}=\text{O}$ and $\text{Mn}=\text{O}$ complexes in the same reaction.³⁵ It is quite significant that the Ni-species displayed such a high rate constant.

44b was also found to be reactive towards ferrocene. Ferrocene (1 equiv. in acetone) reacted with **44b** instantaneously, as evidenced by the disappearance of UV-Vis features attributed to **44b**, and new features in the visible region that can be attributed to ferrocenium cation ($\lambda_{\text{max}} = 630 \text{ nm}$, fig. A.9). The conversion of ferrocene to ferrocenium was quantitative. **44b** thus represents an exciting example of a terminal Ni-oxygen adduct that is capable of HAA, OAT and electron transfer.

2.4 Conclusions

In summary, a Ni^{III} complex, **44b**, was generated by the one-electron oxidation of **44a** at low temperature. EPR spectroscopy suggested the oxidation was borne principally by the central metal atom, yielding a low-spin ($S = 1/2$), d^7 Ni^{III} ion, sitting in a square planar coordination environment. XAS analysis provided further support for this indicating that **44b** contained a Ni^{III} centre coordinated by four N/O donor ligands. DFT calculations on the structure and Mulliken spin density supported these experimental conclusions further. **44b** was capable of oxidizing organic substrates including 2,6-DTBP, BNAH, and PPh_3 . This constituted the first example of a terminal $\text{Ni}^{\text{III}}\text{-O(X)}$ species that is sufficiently well-behaved to allow thorough structural, spectroscopic, and reactivity investigations, and was an important step towards the elucidation of the properties of these compounds and their role in oxidation catalysis.

2.5 Experimental section

Physical Methods

Electronic absorption spectra were recorded on a HewlettPackard (Agilent) 8453 diode array spectrophotometer (190-1100 nm range) in quartz cuvettes cooled using a liquid nitrogen cooled cryostat from Unisoku Scientific Instruments (Osaka, Japan). ^1H and ^{31}P NMR analyses were performed on a Bruker Avance III 400 MHz instrument. GC-MS was performed using a GCT Premier Micromass time of flight mass spectrometer (TOF). ESI mass spectra were acquired using a Micromass time of flight spectrometer (TOF), interfaced to a Waters 2690 HPLC. EPR spectra were recorded on a Magnetechn Miniscope MS2000 instrument, with liquid nitrogen cooling.

Materials and synthesis

All reactions with air-sensitive materials were conducted under an inert atmosphere using either standard Schlenk techniques or a nitrogen atmosphere glove box. All reagents and solvents were purchased from commercial sources and used as received, unless otherwise stated. Anhydrous DMF and acetonitrile were purchased and used without further purification. Anhydrous THF and diethyl ether were dispensed through an Innovative Technology PureSolv EN solvent purification system and deoxygenated by purging with argon. Acetone was dried over magnesium sulfate, then over 4 Å molecular sieves, distilled and deoxygenated by purging with argon.

$[\text{Ni}^{\text{II}}(\text{OH})(\text{pyN}_2^{\text{Me}_2})]^-$ was prepared according to the reported procedure⁶ and recrystallized from DMF/diethyl ether. Its identity was confirmed by ^1H NMR, UV-Vis and ATR-FTIR spectroscopies, and its stability in acetone solutions verified by ^1H NMR spectroscopy. The $[\text{D}_6]$ acetone spectrum displays minor solvent shifts compared to the reported CD_2Cl_2 spectrum. Moreover, the proton signal at -4.89 ppm signifies the integrity of the hydroxo moiety.

δH (400 MHz, $[\text{D}_6]$ acetone): 8.00 (1H, t, 4-py), 7.49 (2H, d, 3,5-py), 6.85 (4H, d, ArH), 6.77 (2H, t, ArH), 3.45 (8H, m, NCH_2CH_3), 2.50 (12H, s, CH_3), 1.35 (12H, m, NCH_2CH_3), -4.89 (1H, s, OH).

Solutions of **44a** were obtained by exposing $[\text{Ni}^{\text{II}}(\text{OH})(\text{pyN}_2^{\text{Me}_2})]^-$ to CO_2 according to the reported procedures,⁶ and they were either used directly or the compound was isolated by crystallisation. The ^1H NMR spectrum of **44a** in $[\text{D}_6]$ acetone differs from that of $[\text{Ni}^{\text{II}}(\text{OH})(\text{pyN}_2^{\text{Me}_2})]^-$ by the absence of the OH signal.

δ H (400 MHz, [D₆]acetone): 8.09 (1H, t, 4-py), 7.50 (2H, d, 3,5-py), 6.85 (4H, d, ArH), 6.77 (2H, t, ArH), 3.42 (8H, m, NCH₂CH₃), 2.52 (12H, s, CH₃), 1.39 (12H, m, NCH₂CH₃).

Deutero-2,6-di-*tert*-butylphenol

Deutero-2,6-di-*tert*-butylphenol was prepared as follows according to a modification of the reported literature procedure.³⁶

1.030 g of 2,6-di-*tert*-butylphenol (5.0 mmol) was stirred with 2 mL of deuterium oxide for 24 h, whilst heating above its melting point (45°C). The mixture was then allowed to cool down and the phenol extracted into 4 mL of hexane. The solution was dried over magnesium sulfate and the solvent removed *in vacuo*. The cycle was repeated with 2 mL of fresh D₂O, and the product was obtained as a white solid (0.820 g, 80%). The degree of incorporation of deuterium (95%) was evaluated via ¹H NMR, by the decrease of the intensity of the OH peak at 5.22 ppm (in anhydrous CD₃Cl).

Preparation of [Ni^{III}(OCO₂H)(pyN₂^{Me₂})], hydrogenocarbonato-*N,N'*-bis(2,6-dimethylphenyl)-2,6-pyridinedicarboxamido-nickel(III), **44b**

A 0.4 mM solution of **44a** in acetone was cooled in a cuvette cooled to -80 °C (or -40°C). 52 μL of a freshly prepared 15 mM solution of magic blue in acetonitrile was added under continuous stirring. The formation of **44b** was immediate as evidenced by the formation of bands at 520 and 790 nm.

EPR analysis

A 0.4 mM solution of **44b** for EPR analysis was prepared according to the above procedure. An aliquot was transferred, via a pre-cooled pipette, into a pre-cooled quartz EPR tube and frozen in liquid nitrogen. The EPR spectrum was recorded at 113 K, 9.387 GHz, 31.6 W microwave power, with a 300 mT field sweep in 60 s, and 0.5 mT field modulation amplitude. Integration, simulation and fitting were executed with Matlab and the easySpin computational package.³⁷ The system was modelled as an S = ½ electron spin with axial *g* tensor, and inhomogeneous line broadening. Quantification of the concentration of spins in the sample was determined by comparison of the double integral of the signal of **44b** to that of a frozen 0.4 mM acetone solution of TEMPO, measured under the same conditions.

X-Ray absorption spectroscopy

Samples for XAS analysis were prepared by transferring acetone solutions of **44a** (4 mM) and **44b** (1.6 mM) into XAS sample cups pre-cooled in a liquid nitrogen bath and immediately freezing them. The solution of **44b** was prepared by the slow addition of 0.5 mL of a freshly prepared 10 mM solution of magic blue in acetone to 2 mL of a 2 mM solution of **44a** cooled to -80 °C. The lower concentration of **44b** was due to limited solubility at low temperature.

XAS Data Collection & Analysis

XAS data was collected on beamline X3B at the National Synchrotron Light Source (Brookhaven National Laboratory, Upton, NY USA). The beamline was equipped with a Si(111) double crystal monochromator with sagittal focusing of the second crystal for energy selection, and a downstream cylindrically bent nickel-coated mirror for vertical focusing and harmonic rejection. Samples were maintained at approx. 15-20 K using a He Displex cryostat. A Ni metal foil was used for internal energy calibration, with the first inflection point of the reference foil set to 8333 eV. XAS data were collected in fluorescence using a 31-element solid state germanium detector (Canberra), with a Co filter (3 absorption lengths) used to reduce scatter and maintain detector linearity. Data was obtained over an energy range of 8133 – 9090 eV. Samples were carefully monitored for evidence of photoreduction during data collection, with no evidence of radiation damage based on the absence of a red-shift in the experimental absorption edge. Averaging and normalization of the XAS data was performed using Athena, a graphical implementation of the IFEFFIT package. Reference spectra were carefully aligned to ensure accurate energy calibrations for both **44a** and **44b**. EXAFS analysis was carried out with Artemis, using theoretical phase and amplitude parameters calculated with FEFF6L for the crystal structure of **44a** as an initial model. The structure of the FEFF6L input model was adjusted as needed to match the refined bond lengths from EXAFS analysis. In a given EXAFS fit, r and σ^2 were allowed to freely float, while coordination number n for a given shell was fixed and varied in integral steps. The scale factor S_0 was fixed at 0.9, while ΔE_0 (the point at which $k = 0 \text{ \AA}^{-1}$) was allowed to float at a common value for all shells. The goodness of fit was assessed using the R -factor fit statistic reported by IFEFFIT, which is defined as $R = \sum[(\chi_{data} - \chi_{theory})^2 / (\chi_{data})^2]$.

First shell EXAFS analysis of **44a** indicates fit 2.2, consisting of 4 Ni-N/O scatterers at 1.87 Å, is the best fit based on resolution, GOF, and BVS grounds. It is possible to split

Table 2.2. First-shell EXAFS fits for **44a** and **44b**.^[a]

Complex 44a									
fit	Ni-O/N			Ni-N/O			R	ΔE_0	BVS
	<i>n</i>	<i>r</i>	σ^2	<i>n</i>	<i>r</i>	σ^2			
2.1				3	1.87	1.7	0.0529	0.41	1.70
2.2				4	1.87	3.1	0.0170	-0.42	2.27
2.3				5	1.87	4.3	0.0134	-1.25	2.84
2.4				6	1.87	5.5	0.0296	-2.08	3.42
2.5	1	1.79	0.5	3	1.90	1.8	0.0130	-0.19	2.28
2.6	2	1.82	3.1	2	1.90	2.0	0.0153	-0.77	2.35
2.7	2	1.82	10.5	3	1.87	2.4	0.0161	-2.49	3.01
2.8	1	1.79	12.9	4	1.87	3.2	0.0129	-2.30	2.99

Complex 44b									
fit	Ni-O/N			Ni-N/O			R	ΔE_0	
	<i>n</i>	<i>r</i>	σ^2	<i>n</i>	<i>r</i>	σ^2			
3.1				3	1.89	4.5	0.0844	-1.84	
3.2				4	1.89	6.3	0.0367	-2.25	
3.3				5	1.89	8.0	0.0191	-2.78	
3.4				6	1.89	9.5	0.0192	-3.32	
3.5	1	1.82	0.9	3	1.95	5.9	0.0112	0.85	
3.6	2	1.84	2.9	2	1.99	4.8	0.0093	0.65	
3.7	2	1.97	5.3	3	1.86	3.7	0.0029	-0.32	
3.8	1	2.02	1.8	4	1.88	4.4	0.0022	-0.12	

[a] The bolded row represents the best fit for each system. Fitting range was $k = 1.5$ - $13.5 \text{ \AA}^{-1}$ for **44a** (resolution = $0.13 \text{ \AA}$, back transform = 1 - $2 \text{ \AA}$), $k = 1.5$ - $13 \text{ \AA}^{-1}$ for **44b** (resolution = $0.137 \text{ \AA}$, back transform range = 1 - $1.95 \text{ \AA}$). r is in units of $\text{\AA}$; σ^2 is in units of $10^{-3} \text{ \AA}^2$; ΔE_0 is in units of eV; R represents the goodness of the fit (GOF) and is defined as $R = \sum [(\chi_{data} - \chi_{theory})^2 / (\chi_{data})^2]$. The bond valence sum (BVS) was calculated for **44a** and is defined as $BVS = \sum e^{\frac{r_0 - r}{0.37}}$, where r_0 is an empirically derived parameter for a given pair of atoms and r is the actual bond length. The values of r_0 were taken from reference.⁶

the first shell into two subshells (e.g., fit 2.5), but the difference in path lengths is generally smaller than the 0.13 Å resolution of the data. For **44b**, single shell fits revealed significantly increased disorder based on the magnitude of σ^2 . Splitting this shell into two sub-shells results in a significantly improved fit quality (e.g., fit 3.6). Notably, fits to a 5-coordinate Ni^{III} site in **44b**, while giving outstanding *R*-factor values, deviate significantly from the structural model and are difficult to reproduce accurately, suggesting that they are not plausible global minima, unlike the two-shell 4-coordinate fits.

DFT Methods

All calculations have been performed using the Amsterdam Density Functional (ADF, version 2013.01)^{38,39} and QUILD⁴⁰ programs. The S12g density functional⁴¹ was used for obtaining the molecular structures since it provides reliable spin-state energies and gives structures with equal accuracy as the PBE-D^{42,43} functional, which was successfully used recently for a set of 16 Fe^{III/IV} (oxo/peroxo/hydroxo) complexes.⁴⁴ The frozen core approach³⁹ with a triple- ζ basis set with double polarization (TZ2P) was used for the geometry optimizations. Scalar relativistic effects were taken into account self-consistently (ZORA). Solvent effects were included in all calculations through the use of COSMO^{45,46} with parameters corresponding to the solvent used experimentally (acetone). Accurate numerical integration settings with the Becke grid⁴⁷ were used in all calculations.

Reactivity Studies

General procedure for reactivity experiments

A solution of **44b** at -80 °C (or -40 °C) was prepared according to the above procedure. Substrates were added as concentrated acetone solutions. The reactions were monitored using UV-Vis spectroscopy, and after complete disappearance of the features corresponding to **44b**, were allowed to warm up to room temperature. The reaction mixtures were diluted with methanol for MS analysis, or the solvent was removed *in vacuo* for NMR analysis.

Rate constants determination

Reactions were executed with 7 to 300 equivalents of substrate to ensure pseudo-first order conditions. The second-order rate constant was determined from the linear dependence of

the pseudo-first order constant on substrate concentration. Values for the observed k_{obs} were obtained by fitting the decay of the absorbance at 520 nm during a reaction as an exponential. The average from repeated experiments were utilized for the determination of k_2 .

References

- (1) Pirovano, P.; Farquhar, E. R.; Swart, M.; Fitzpatrick, A. J.; Morgan, G. G.; McDonald, A. R. *Chem. Eur. J.* **2015**, *21*, 3785–3790.
- (2) Chmielewski, P. J.; Latos-Grażyński, L. *Inorg. Chem.* **1997**, *36*, 840–845.
- (3) Chiou, T.-W.; Liaw, W.-F. *Inorg. Chem.* **2008**, *47*, 7908–7913.
- (4) Zhou, W.; Schultz, J. W.; Rath, N. P.; Mirica, L. M. *J. Am. Chem. Soc.* **2015**, *137*, 7604–7607.
- (5) Pfaff, F. F.; Heims, F.; Kundu, S.; Mebs, S.; Ray, K. *Chem. Commun.* **2012**, *48*, 3730–3732.
- (6) Huang, D.; Holm, R. H. *J. Am. Chem. Soc.* **2010**, *132*, 4693–4701.
- (7) Huang, D.; Makhlynets, O. V.; Tan, L. L.; Lee, S. C.; Rybak-Akimova, E. V.; Holm, R. H. *Proc. Natl. Acad. Sci. U.S.A.* **2011**, *108*, 1222–1227.
- (8) Huang, D.; Makhlynets, O. V.; Tan, L. L.; Lee, S. C.; Rybak-Akimova, E. V.; Holm, R. H. *Inorg. Chem.* **2011**, *50*, 10070–10081.
- (9) Troeppner, O.; Huang, D.; Holm, R. H.; Ivanović-Burmazović, I. *Dalton Trans.* **2014**, *43*, 5274–5279.
- (10) Bell, F. A.; Ledwith, A.; Sherrington, D. C. *J. Chem. Soc. C* **1969**, 2719–2720.
- (11) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877–910.
- (12) Patra, A. K.; Mukherjee, R. *Inorg. Chem.* **1999**, *38*, 1388–1393.
- (13) Lappin, A. G.; Laranjeira, M. C. M.; Peacock, R. D. *Inorg. Chem.* **1983**, *22*, 786–791.
- (14) Jacobs, S. A.; Margerum, D. W. *Inorg. Chem.* **1984**, *23*, 1195–1201.
- (15) Kruger, H. J.; Holm, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 2955–2963.
- (16) Kruger, H. J.; Peng, G.; Holm, R. H. *Inorg. Chem.* **1991**, *30*, 734–742.
- (17) Corker, J. M.; Evans, J.; Levason, W.; Spicer, M. D.; Andrews, P. *Inorg. Chem.* **1991**, *30*, 331–334.
- (18) Lee, Y.-M.; Hong, S.; Morimoto, Y.; Shin, W.; Fukuzumi, S.; Nam, W. *J. Am. Chem. Soc.* **2010**, *132*, 10668–10670.
- (19) Cao, T.-P.-A.; Nocton, G.; Ricard, L.; Le Goff, X. F.; Auffrant, A. *Angew. Chem. Int. Ed.* **2014**, *53*, 1368–1372.
- (20) Lovecchio, F. V.; Gore, E. S.; Busch, D. H. *J. Am. Chem. Soc.* **1974**, *96*, 3109–3118.
- (21) Haines, R.; McAuley, A. *Coord. Chem. Rev.* **1981**, *39*, 77–119.
- (22) Stuart, J. N.; Goerges, A. L.; Zaleski, J. M. *Inorg. Chem.* **2000**, *39*, 5976–5984.
- (23) Haines, R. I.; McAuley, A. *Inorg. Chem.* **1980**, *1109*, 719–723.
- (24) Alonso, P. J.; Falvello, L. R.; Forniés, J.; Martín, A.; Menjón, B.; Rodríguez, G. *Chem. Commun.* **1997**, *2*, 503–504.
- (25) Collins, T. J.; Nichols, T. R.; Uffelman, E. S. *J. Am. Chem. Soc.* **1991**, *113*, 4708–4709.
- (26) Ottenwaelder, X.; Ruiz-García, R.; Blondin, G.; Carasco, R.; Cano, J.; Lexa, D.; Journaux, Y.; Aukaaloo, A. *Chem. Commun.* **2004**, 504–505.
- (27) Kundu, S.; Pfaff, F. F.; Miceli, E.; Zaharieva, I.; Herwig, C.; Yao, S.; Farquhar, E. R.; Kuhlmann, U.; Bill, E.; Hildebrandt, P.; Dau, H.; Driess, M.; Limberg, C.; Ray, K. *Angew. Chem. Int. Ed.* **2013**, *52*, 5622–5626.
- (28) Colpas, G. J.; Maroney, M. J.; Bagyinka, C.; Kumar, M.; Willis, W. S.; Suib, S. L.; Mascharak, P. K.; Baidya, N. *Inorg. Chem.* **1991**, *30*, 920–928.
- (29) Cho, J.; Kang, H. Y.; Liu, L. V.; Sarangi, R.; Solomon, E. I.; Nam, W. *Chem. Sci.* **2013**, *4*, 1502–1508.
- (30) Haumann, M.; Porthun, A.; Buhrke, T.; Liebisch, P.; Meyer-Klaucke, W.; Friedrich, B.; Dau, H. *Biochemistry* **2003**, *42*, 11004–11015.
- (31) Davidson, G.; Choudhury, S. B.; Gu, Z.; Bose, K.; Roseboom, W.; Albracht, S. P. J.; Maroney, M. J. *Biochemistry* **2000**, *39*, 7468–7479.
- (32) Sarangi, R. *Coord. Chem. Rev.* **2013**, *257*, 459–472.
- (33) Altwicker, E. R. *Chem. Rev.* **1967**, *67*, 475–531.
- (34) Wittman, J. M.; Hayoun, R.; Kaminsky, W.; Coggins, M. K.; Mayer, J. M. *J. Am. Chem. Soc.* **2013**, *135*, 12956–12959.
- (35) Sastri, C. V.; Park, M. J.; Ohta, T.; Jackson, T. A.; Stubna, A.; Seo, M. S.; Lee, J.; Kim, J.; Kitagawa, T.; Münck, E.; Que, L.; Nam, W. *J. Am. Chem. Soc.* **2005**, *127*, 12494–12495.

- (36) Kurahashi, T.; Kikuchi, A.; Shiro, Y.; Hada, M.; Fujii, H. *Inorg. Chem.* **2010**, *49*, 6664–6672.
- (37) Stoll, S.; Schweiger, A. *J. Magn. Reson.* **2006**, *178*, 42–55.
- (38) Baerends, E. J. et al. ADF2013.01.; SCM, Amsterdam, 2013.
- (39) Te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Fonseca Guerra, C.; van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931–967.
- (40) Swart, M.; Bickelhaupt, F. M. *J. Comput. Chem.* **2008**, *29*, 724–734.
- (41) Swart, M. *Chem. Phys. Lett.* **2013**, *580*, 166–171.
- (42) Grimme, S. *J. Comput. Chem.* **2006**, *27*, 1787–1799.
- (43) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- (44) Swart, M. *Chem. Commun.* **2013**, *49*, 6650–6652.
- (45) Klamt, A.; Schüürmann, G. *J. Chem. Soc., Perkin Trans. 2* **1993**, 799–805.
- (46) Pye, C. C.; Ziegler, T. *Theor. Chem. Acc.* **1999**, *101*, 396–408.
- (47) Franchini, M.; Philipsen, P. H. T.; Visscher, L. *J. Comput. Chem.* **2013**, *34*, 1819–1827.

Chapter 3

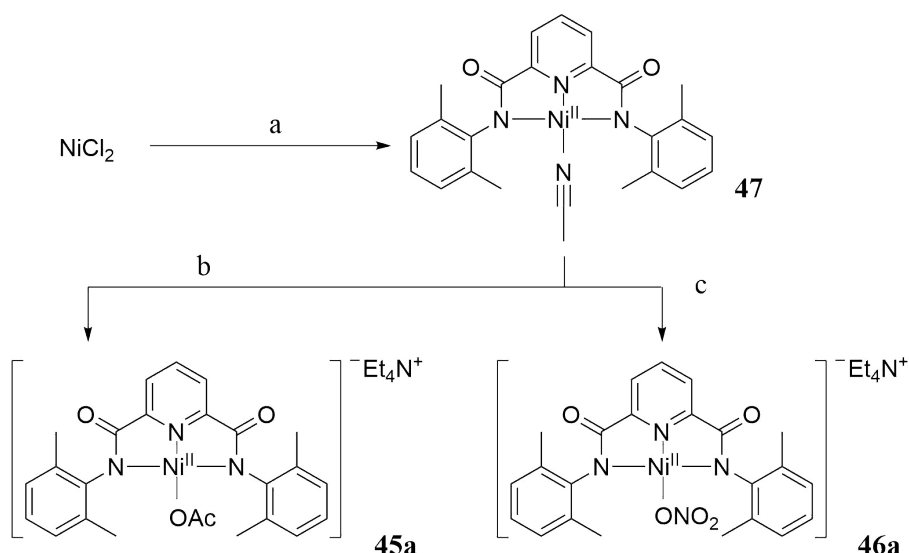
Tuning of the Reactivity of Nickel(III)–Oxygen Adducts in O–H and C–H Bond Activation

The work described in this chapter has been previously published in an article in *Journal of the American Chemical Society*.¹ The DFT calculations were performed by Prof. Marcel Swart (University of Girona, Spain); the XAS data collection and analysis were done by Dr Eric R. Farquhar (Brookhaven National Laboratory, USA); Dr. A. J. Fitzpatrick and Prof. Grace G. Morgan (University College Dublin) kindly allowed use of the EPR spectrometer and helped with spectra acquisition; the XRD data collection and structure solutions and refinements were done by Dr Brendan Twamley (Trinity College Dublin).

Reproduced in part with permission from: Pirovano, P.; Farquhar, E. R.; Swart, M.; McDonald, A. R. *J. Am. Chem. Soc.* **2016**, 138, 14362– 14370. Copyright 2016 American Chemical Society.

3.1 Introduction

While the preparation of the $\text{Ni}^{\text{III}}\text{-OCO}_2\text{H}$ complex **44b** was an exciting achievement, only its reaction with easily oxidised substrates, such as phenols and the H^- donor BNAH, could be probed; its limited thermal stability prevented more in-depth examinations of the reaction mechanisms, and of more arduous reactions such as the oxidation of hydrocarbons. Moreover, **44b** represented the first example of a metal-bicarbonate oxidant, and suggested that the properties of $\text{Ni}^{\text{III}}\text{-O-X}$ species could easily be varied by substitution of the O ligand. Analogous compounds to **44a**, with different O- donor ligands in place of bicarbonate, could be easily synthesised. In this chapter, the preparation of two new $\text{Ni}^{\text{III}}\text{-O-X}$ complexes, $[\text{Ni}^{\text{III}}(\text{OAc})(\text{pyN}_2^{i\text{Pr}_2})]$ (**45b**) and $[\text{Ni}^{\text{III}}(\text{ONO}_2)(\text{pyN}_2^{i\text{Pr}_2})]$ (**46b**), from their $\text{Ni}^{\text{II}}\text{-O-X}$ precursors **45a** and **46a**, respectively (sch. 3.1) is described. An investigation into relationships between the properties of the O-donor ligands in **44-46b** and their oxidative reactivity is presented.



Scheme 3.1. Synthesis of Ni^{II} complexes **45a**, **46a**, and **47**. (a) 1) $\text{H}_2\text{pyN}_2^{\text{Me}_2}$, CH_3OH , 65°C ; 2) NaOCH_3 ; 3) CH_3CN (b) Et_4NOAc , CH_3CN , Et_2O , room temperature; (c) Et_4NNO_3 , CH_3CN , Et_2O , room temperature.

3.2 Synthesis and characterisation of nickel(II) complexes

$\text{Et}_4\text{N}[\text{Ni}^{\text{II}}(\text{OAc})(\text{pyN}_2^{\text{Me}_2})]$ (**45a**) and $\text{Et}_4\text{N}[\text{Ni}^{\text{II}}(\text{ONO}_2)(\text{pyN}_2^{\text{Me}_2})]$ (**46a**) were obtained via a two-step synthesis (sch. 3.1). The neutral complex $[\text{Ni}^{\text{II}}(\text{CH}_3\text{CN})(\text{pyN}_2^{\text{Me}_2})]$ (**47**) was

first synthesized by reacting $\text{H}_2\text{pyN}_2^{\text{Me}_2}$ with NiCl_2 (1 equiv.) in the presence of NaOCH_3 (2.1 equiv.), in CH_3OH . Subsequent CH_3CN ligand introduction and filtration of insoluble by-products allowed for isolation of pure **47**. The product was obtained in 75% yield. The CH_3CN ligand in **47** could be displaced by the addition of either tetraethylammonium acetate (Et_4NOAc , 1.1 equiv.) to a CH_3CN solution of **47**, or tetraethylammonium nitrate (Et_4NNO_3 , 1.1 equiv.) to a CH_3OH solution of **47**, to yield **45a** and **46a**, respectively. ^1H and ^{13}C NMR, ATR-FTIR, and ESI MS confirmed the structure, composition, and elemental assignments of the complexes.

Single crystals of **45a**, **46a** and **47**, that were suitable for X-ray diffraction (XRD) measurements were obtained (fig. 3.1). All the complexes showed the Ni^{II} ion to be in a square planar coordination environment. The geometric parameters of the $[\text{Ni}^{\text{II}}(\text{pyN}_2^{\text{Me}_2})]$ unit were similar to those of previously reported $[\text{Ni}^{\text{II}}(\text{pyN}_2^{\text{Me}_2})]$ complexes (table 3.3).² The ^-OAc and $^-\text{ONO}_2$ anions, in **45a** and **46a**, respectively, bind in a monodentate fashion (fig. 3.1), similarly to the bicarbonate ligand in **44a**,² and lie perpendicular to the $[\text{Ni}(\text{pyN}_2^{\text{Me}_2})]$ plane. The XRD experiments confirmed the structure of compounds **45a**, **46a** and **47**, showing a nearly invariant square planar nickel coordination environment, with bond distances that are largely unaffected by the electron-donating ability of the ancillary ligands.

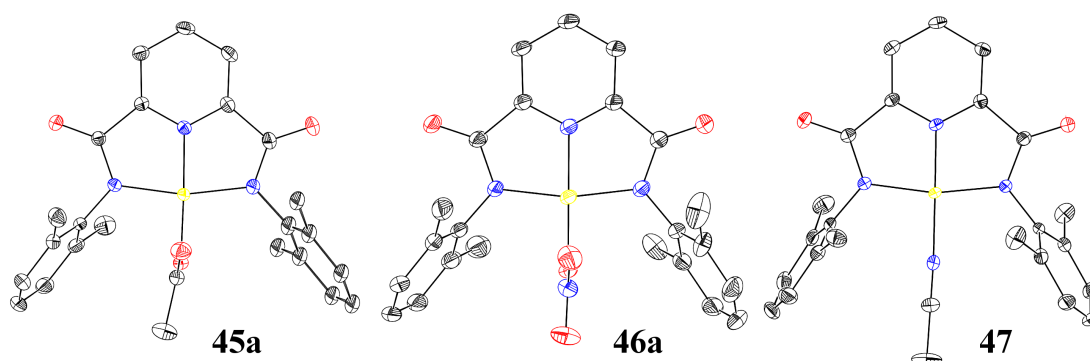
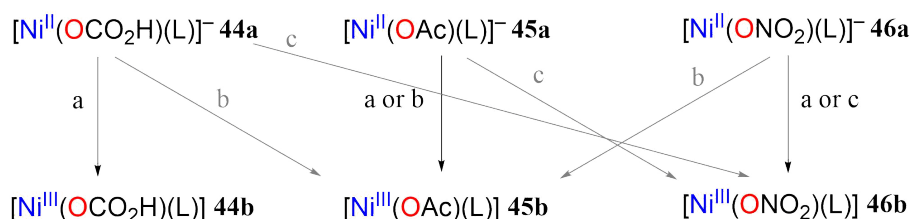


Figure 3.1. ORTEP plots (at 50% probability level) of the x-ray crystallographically-determined structures of **45a**, **46a**, and **47**; hydrogen atoms for all and counterions for **45a** and **46a**, have been omitted for clarity.

3.3 Formation and characterisation of nickel(III) complexes

The generation of $[\text{Ni}^{\text{III}}(\text{OCO}_2\text{H})(\text{pyN}_2^{\text{Me}_2})]$, **44b**, by the one electron oxidation of **44a**, was reported in chapter 2. In an analogous fashion, complexes **45a** and **46a** were oxid-

ized to yield $[\text{Ni}^{\text{III}}(\text{OAc})(\text{pyN}_2^{\text{Me}_2})]$ and $[\text{Ni}^{\text{III}}(\text{ONO}_2)(\text{pyN}_2^{\text{Me}_2})]$, **45-46b** respectively (sch. 3.2). This was achieved by dissolving **45a** and **46a** in acetone (0.3 mM) and cooling these solutions to $-40\text{ }^\circ\text{C}$. Addition of one equivalent of the one-electron oxidant tris(4-bromophenyl)ammoniumyl hexachloroantimonate (magic blue, dissolved in CH_3CN), caused an immediate reaction as evidenced by electronic absorption spectroscopy (fig. 3.2). For both **45a** and **46a** the immediate appearance of two intense visible and NIR absorption bands in the electronic absorption spectrum, assigned to **45b** and **46b** respectively, demonstrated their one-electron oxidation.



Scheme 3.2. Synthetic routes to the Ni^{III} complexes **44-46b**. (a) magic blue (1 equiv., acetone); (b) $\text{NaOCl}/\text{AcOH}/\text{H}_2\text{O}$ (15 equiv., acetone); (c). $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$ (CAN, 5 equiv., acetone). Grey crossover reactions show that NaOCl/AcOH always yields **45b**, and CAN always yields **46b**.

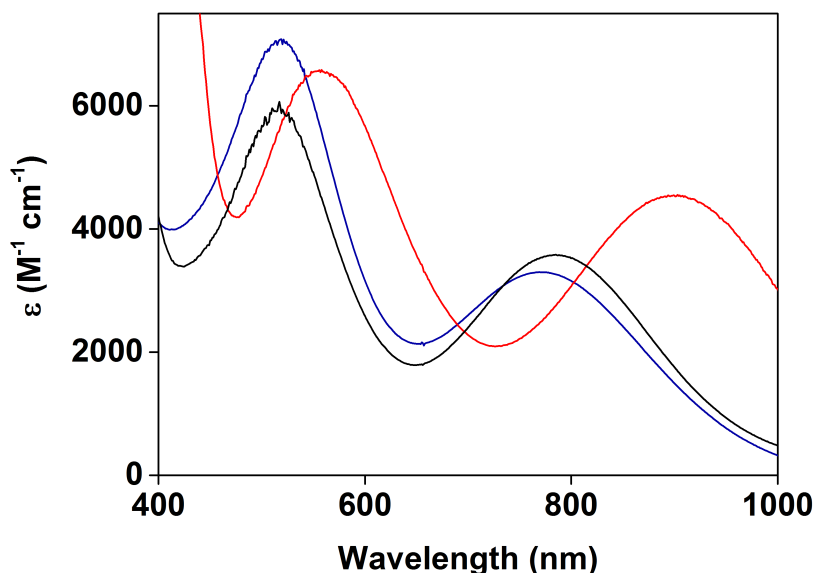


Figure 3.2. UV-visible spectra of $[\text{Ni}^{\text{III}}(\text{OX})(\text{pyN}_2^{\text{Me}_2})]$ complexes **44b** (black trace), **45b** (blue trace), and **46b** (red trace), in acetone solutions. Molar absorptivities were calculated using the Beer-Lambert equation from the measured absorbances and EPR-determined concentrations of the products.

Table 3.1. Salient spectroscopic features and properties of [Ni^{II}(pyN₂^{Me}₂)] and [Ni^{III}(OX)(pyN₂^{Me}₂)].

	λ_{max} (nm) (ϵ / M ⁻¹ cm ⁻¹)	$\nu_{C=O/C\equiv N/N=O}$ (cm ⁻¹)	$g_{\perp}, g_{\parallel}$ ($g_{av.}$)	$E_{1/2}$ vs Fc ⁺ /Fc (V)	Ni–O (Å)	Ni K-pre-edge, edge (eV)	k_2 2,6-DTBP at -40 °C (M ⁻¹ s ⁻¹) ^[d]
44a	470 (1200)	1618, 1585		0.48	1.87 ^[a] , 1.878 ^[b] , 1.871(4) ^[c]	8345	
45a	470 (1200)	1620, 1608, 1585		0.35	1.87 ^[a] , 1.864 ^[b] , 1.870(1) ^[c]	8333.1, 8345	
46a	455 (1200)	1623, 1609, 1587, 1290		0.56	1.88 ^[a] , 1.890 ^[b] , 1.888(3) ^[c]	8332.7, 8345	
44b	520 (6000), 780 (3600)		2.25, 2.02 (2.17)		1.84 ^[a] , 1.944/2.146 ^[b,e] , or 1.874 ^[b,f]	8345	0.104
45b	510 (7000), 760 (3600)		2.24, 2.02 (2.17)		1.92 ^[a] , 1.929/2.118 ^[b,e] , or 1.864 ^[b,f]	8333.6, 8345	0.125
46b	560 (6700), 890 (4600)		2.25, 2.01 (2.17)		1.93/2.08 ^[a] , 1.944/2.108 ^[b,e] , or 1.888 ^[b,f]	8333.8, 8345	1.96
47	435 (1400), 550 (110)	2337, 2311, 1630, 1585					

[a] from EXAFS fitting; [b] from DFT; [c] from XRD; [d] second order rate constant for the reaction with 2,6-di-*tert*-butylphenol at -40 °C; [e] d_{z^2} spin-density; [f] d_{xz} spin density.

Such features in the visible region have been identified as typical of Ni^{III} complexes of 2,6-pyridinedicarboxamidate ligands.³ Specifically, **45b** displayed features at λ_{max} = 510 and 760 nm, while **46b** displayed absorption maxima at λ_{max} = 560 and 890 nm (table 3.1). The presence of these features compares favourably to the electronic absorption spectrum of **44b** (λ_{max} = 520 and 780 nm, table 3.1), with only minor differences between the –OCO₂H ligated **44b** and –OAc ligated **45b**. In the case of the more electron-poor –ONO₂-ligated **46b**, red-shifted absorption features (compared to **44b** and **45b**) were observed, presumably as a result of the –ONO₂ ligand being markedly less basic.

It was observed that cerium ammonium nitrate ((NH₄)₂[Ce^{IV}(NO₃)₆], CAN) effected the oxidation of **46a** (0.3 mM acetone solution, -40 °C, 5 equiv. of CAN in CH₃OH) to give **46b** as evidenced by electronic absorption spectroscopy and EPR (figs. A.27 and A.28). Fascinatingly, addition of excess CAN (5 equiv.) to either **44a** or **45a**, also caused the appearance of the characteristic absorption bands of **46b** (λ_{max} = 560 and 890 nm, figs. A.29 and A.30), presumably as a result of the large excess of –ONO₂ anions in CAN.

In a similar way, species **45b** could be generated by oxidizing **45a** with hypochlorous acid (formed from an aqueous NaOCl/AcOH mixture), as evidenced by electronic absorption and EPR spectroscopies (figs. A.31 and A.32). Furthermore, addition of NaOCl/AcOH to **44a** or **46a** resulted in the formation of features similar to those of **45b** (figs. A.33

and A.34). In summary, oxidation of the Ni^{II} precursors **44-46a** by magic blue is a method of general validity, while CAN and NaOCl/AcOH could only cleanly generate –ONO₂-ligated **46b** and –OAc-ligated **45b**, respectively. The formation of anion-ligated complexes for CAN and NaOCl/AcOH is an intriguing observation, given the wide employment of these oxidants to generate terminal metal-oxo species.

44-46b were thermally unstable: at -40 °C, half-lives (*t*_{1/2}) of 90 minutes for **44b** and 200 minutes for **46b** were measured; in contrast, **45b** showed no appreciable decay over the course of several hours at -40 °C. When **45b** was prepared using NaOCl/AcOH it displayed a half-life of 750 s at 25 °C. Neither **44b** nor **46b** were stable at 25 °C.

3.3.1 EPR spectroscopy

EPR spectroscopy analysis of **45-46b** showed the presence of a single *S* = ½ species for each complex (fig. 3.3). The spectra displayed axial symmetry with *g*_⊥ > *g*_∥. The average *g*-values (*g*_{av.}, table 3.1) were consistent with the unpaired electron residing predominantly on the Ni^{III} ion. For **44-46b**, the *g*-values (table 3.1 and figs. A.24 to A.26) are essentially equivalent, and together with the shape of the signal (*g*_⊥ > *g*_∥) are consistent with a low-spin, *d*⁷, Ni^{III} ion in square planar or elongated octahedral coordination environment.⁴⁻⁷ The similarities in *g*-value are consistent with the XAS-determined metal-ligand bond distances being almost equal for **44-46b**, and suggests little to no difference in electronic symmetry at the metal site.

DFT Mulliken spin density calculations were performed and suggested that the unpaired spin in **44-46b** predominantly resides in a metal-based molecular orbital (*d*_{z²}- or *d*_{xz}-like molecular orbitals). Often when *g*_⊥ > *g*_∥, it has been indicative of a *d*_{z²} singly occupied molecular orbital.⁴⁻¹¹ However, one cannot definitively conclude where the unpaired spin density resides, as detailed below. The yields of the *S* = ½ entities were determined to be ~95% (±15%), through comparison with a spin standard (TEMPO, 0.4 mM), based on the concentration of the Ni^{II} starting solutions. This corresponds to a nearly quantitative conversion of the Ni^{II} precursors to Ni^{III}-oxygen adducts.

3.3.2 Mass spectroscopy

ESI MS analysis was conducted by injecting thawed acetone solutions of **45b** and **46b**, immediately after thawing. In the solution of **45b**, a peak at *m*/*Z* = 495 was identified that corresponds to a mass of [**45b** + Li]⁺ (fig. 3.4). For **46b**, a mass peak at *m*/*Z* = 510 was detected (fig. 3.4), which corresponds to [**46b** + H₃O]⁺. The isotopic patterns for the

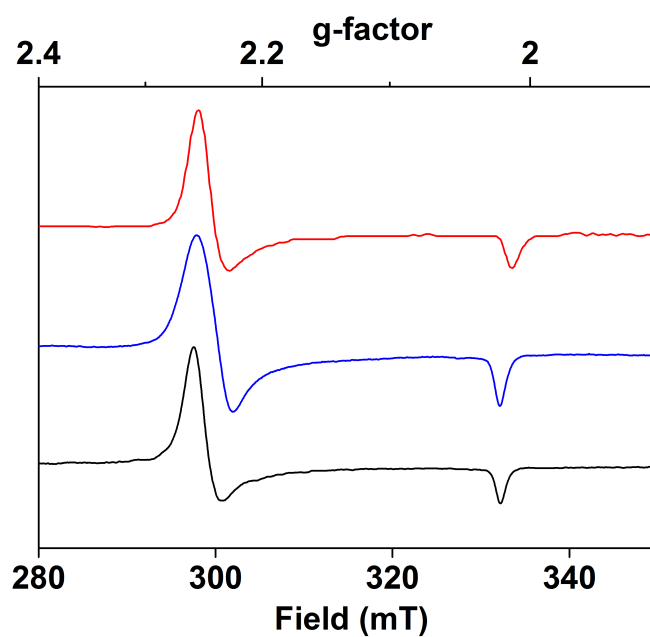


Figure 3.3. EPR spectra of **44b** (black trace), **45b** (blue trace), and **46b** (red trace), collected from frozen acetone solutions at 77 K, microwave power = 31.6 mW. Simulated spectra are in figs. A.24 to A.26.

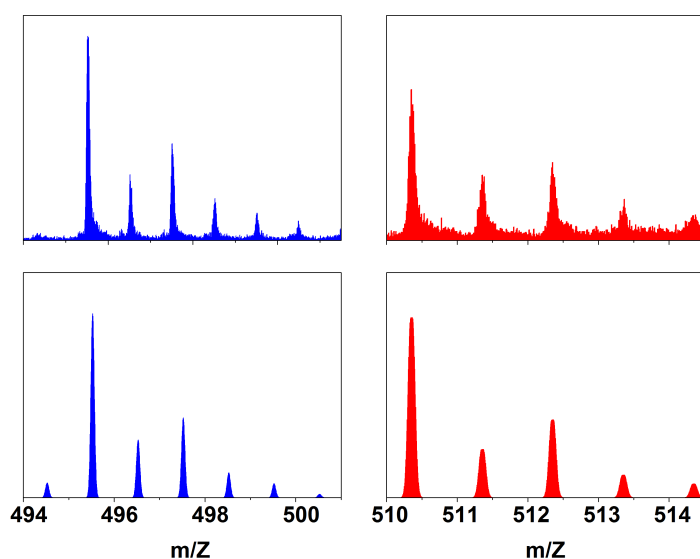


Figure 3.4. ESI MS peaks identified in solutions of **45b** (top left) and **46b** (top right), and simulated isotopic patterns for to $[\mathbf{45b} + \text{Li}]^+$ (bottom left) and $[\mathbf{46b} + \text{H}_3\text{O}]^+$ (bottom right).

observed ions were typical of Ni-containing ions, demonstrating the ions are likely to be the expected Ni^{III} products (simulated spectra in fig. 3.4). It should be noted that in the ESI MS analysis of solutions of the Ni^{II} precursors **45-46a**, only negatively-charged ions could be detected, meaning ESI MS of the Ni^{II} precursor results in the anionic [Ni^{II}(OX)(pyN₂^{Me₂})]⁻ fragment flying. ESI MS analysis of the Ni^{III} products **45-46b** displayed the positively charged ions discussed above. This means that the ESI MS analysis of **45-46b** pertains only to the Ni^{III} oxidation state and not the precursor Ni^{II} species. The low-temperature ESI MS analysis thus provides proof for the elemental composition of **45-46b**.

3.3.3 X-Ray absorption spectroscopy

Neither **45b** nor **46b** were sufficiently thermally stable to grow crystals suitable for X-ray crystallography. Therefore, Ni K-edge X-ray absorption spectroscopy was performed on frozen solutions of both complexes. The Ni K-edge energy obtained for both **45b** and **46b** (8345 eV, table 3.1) was within the range expected for Ni^{III} ions,¹²⁻¹⁴ and was almost the exact same as that obtained for **44b** (8345 eV).

A comparison of the Ni K-edge X-ray absorption near-edge spectra (figs. 3.5 and 3.6) showed little difference between precursor complexes **44-46a**, suggesting that the anionic O-donor ligand does not dramatically affect the Ni K-edge energy (figs. 3.5 and 3.7 and table 3.1). As with a comparison of the XANES of **44a** and **44b** (chapter 2), there was little-to-no shift in the Ni K-edge upon comparison of **45-46a** with **45-46b**, respectively (table 3.1 and fig. 3.7). However, the XANES spectra of Ni^{II} complexes **45-46a** display a markedly different profile/shape to those of **45-46b** (fig. 3.7), indicating a reaction had occurred upon oxidation of **45-46a** to yield **45-46b**. Analogous observations that identify no edge energy changes when comparing Ni^{II/III} species, within comparable coordination environments, have previously been observed.^{12,15,16}

In this instance, contributions to the edge from 1s-to-4p absorption features distort the edge shape (~8340 eV), making determination of nickel oxidation state from edge energy alone challenging. One should further note that the weak 1s-to-3d pre-edge transitions show modest 0.5-1 eV blue shifts (table 3.1 and fig. 3.7) upon conversion of **45a** to **45b** (8333.1 eV to 8333.6 eV) and **46a** to **46b** (8332.7 eV to 8333.8 eV), providing further evidence for an altered ligand field in **45-46b** consistent with an increase in Ni oxidation state.¹⁷

Extended X-ray absorption fine structure (EXAFS) analysis of **45b** and **46b** showed that both contained a first coordination sphere with 4 - 5 O/N scatterers (table 3.1). For **44-46b**, there was a small but statistically significant expansion of the average scatterer distance

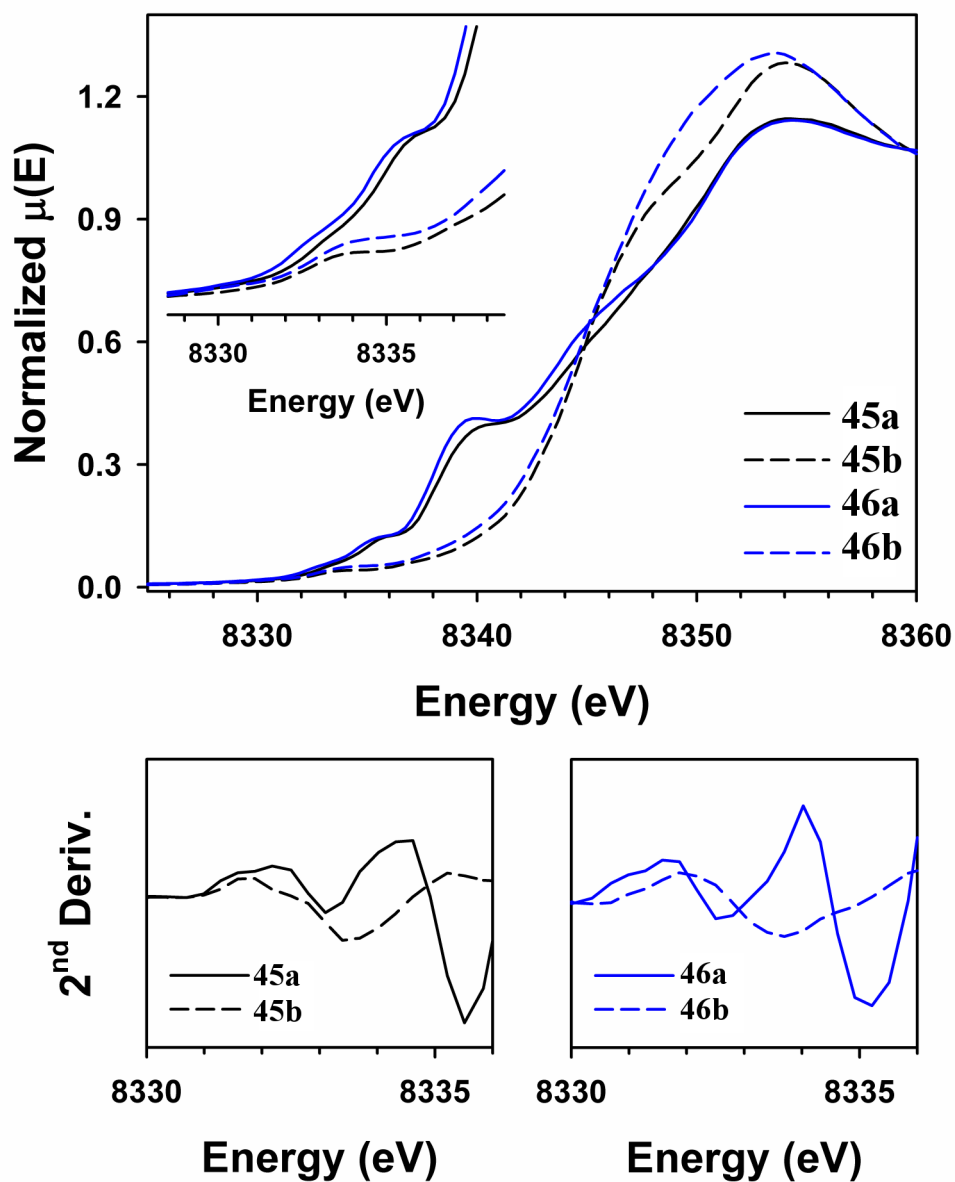


Figure 3.5. Normalized XANES spectra of complexes **45a**, **45b**, **46a**, and **46b**. The inset shows an expansion of the pre-edge region.

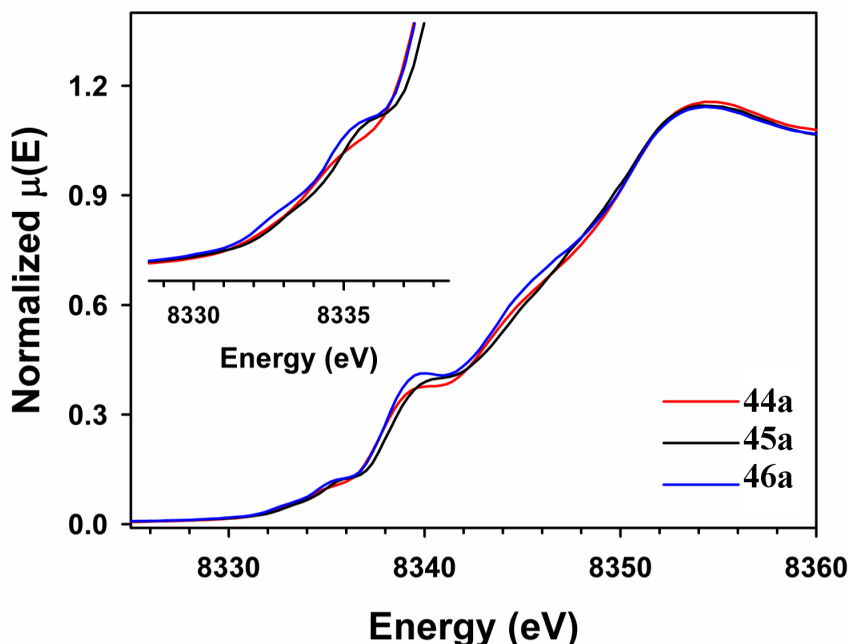


Figure 3.6. Normalized XANES spectra of Ni^{II} complexes **45a** and **46a** compared with previously published data on **44a**. The inset shows an expansion of the pre-edge region.

from the absorber in Ni^{III} **44-46b** (the distance gets longer going from **44b** to **46b**). This would suggest the –ONO₂ ligand in **46b** was more weakly bound, and a weaker field donor.

For **46b** the best fits were obtained through splitting the first shell, yielding scattering atoms at 1.93 and a rather long 2.08 Å, respectively. The latter might reflect a –ONO₂ ligand bound in a bidentate fashion in **46b**. In general, however, the EXAFS analysis cannot conclusively distinguish between 4- and a 5- coordinate species for both **45b** and **46b**. Fitting the data with a very short Ni–O bond (ca. 1.65 Å) resulted in very poor fits, eliminating the possibility of **44-46b** being terminal Ni^{III}=O.

3.3.4 DFT calculations

To further understand the structural properties of **45b** and **46b**, DFT calculations were performed using an array of methods. Firstly, the DFT-predicted Ni–O bond lengths for **44-46a** correlated well with the X-ray crystallographically determined bond lengths, and those measured using XAS. For the Ni^{III} complexes **44-46b**, DFT methods suggested negligible difference in relative energy (ca. 1 kcal/mol) for species where the unpaired electron resides in a metal-based d_{xz} - or d_{z^2} -like molecular orbital.

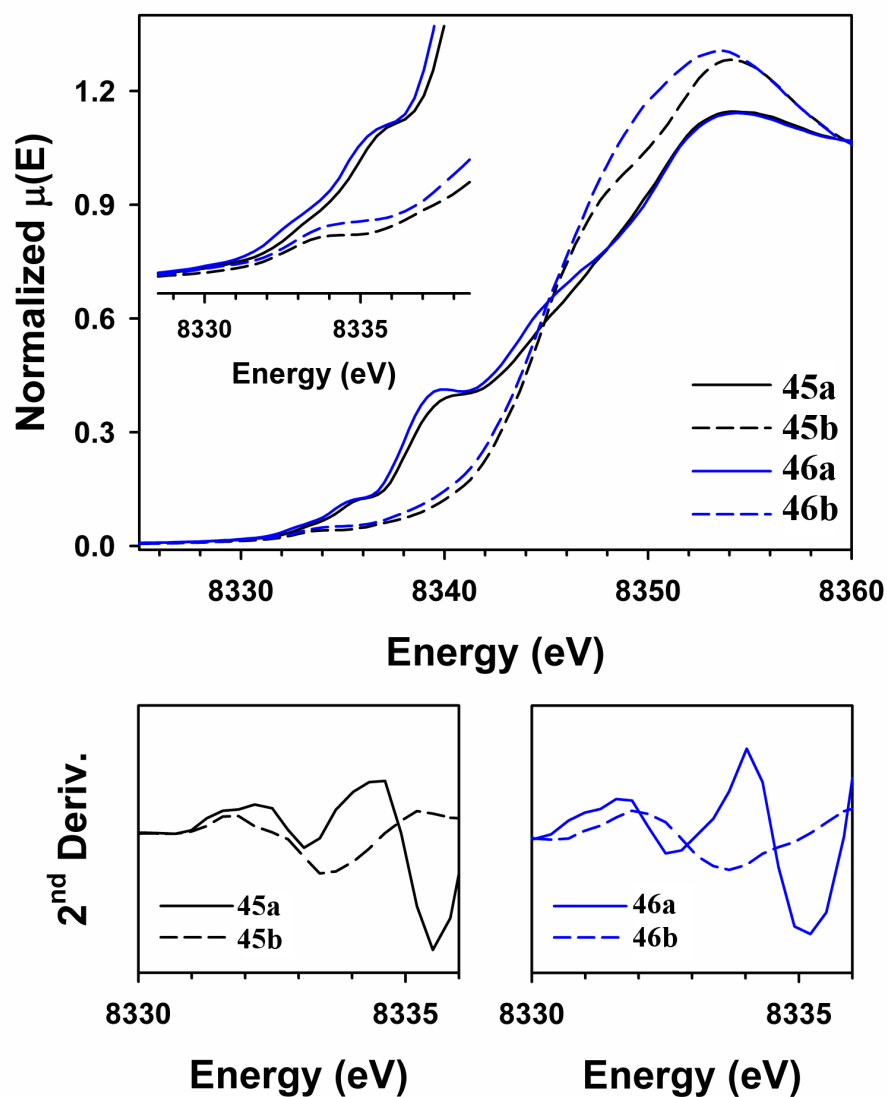


Figure 3.7. (top) Normalized XANES spectra of complexes **45a**, **45b**, **46a**, and **46b**. The inset shows an expansion of the pre-edge region. (bottom) The 2nd derivative of the pre-edge region for complexes **45a**, **45b**, **46a**, and **46b**, highlighting changes in the $1s$ -to- $3d$ transition energy.

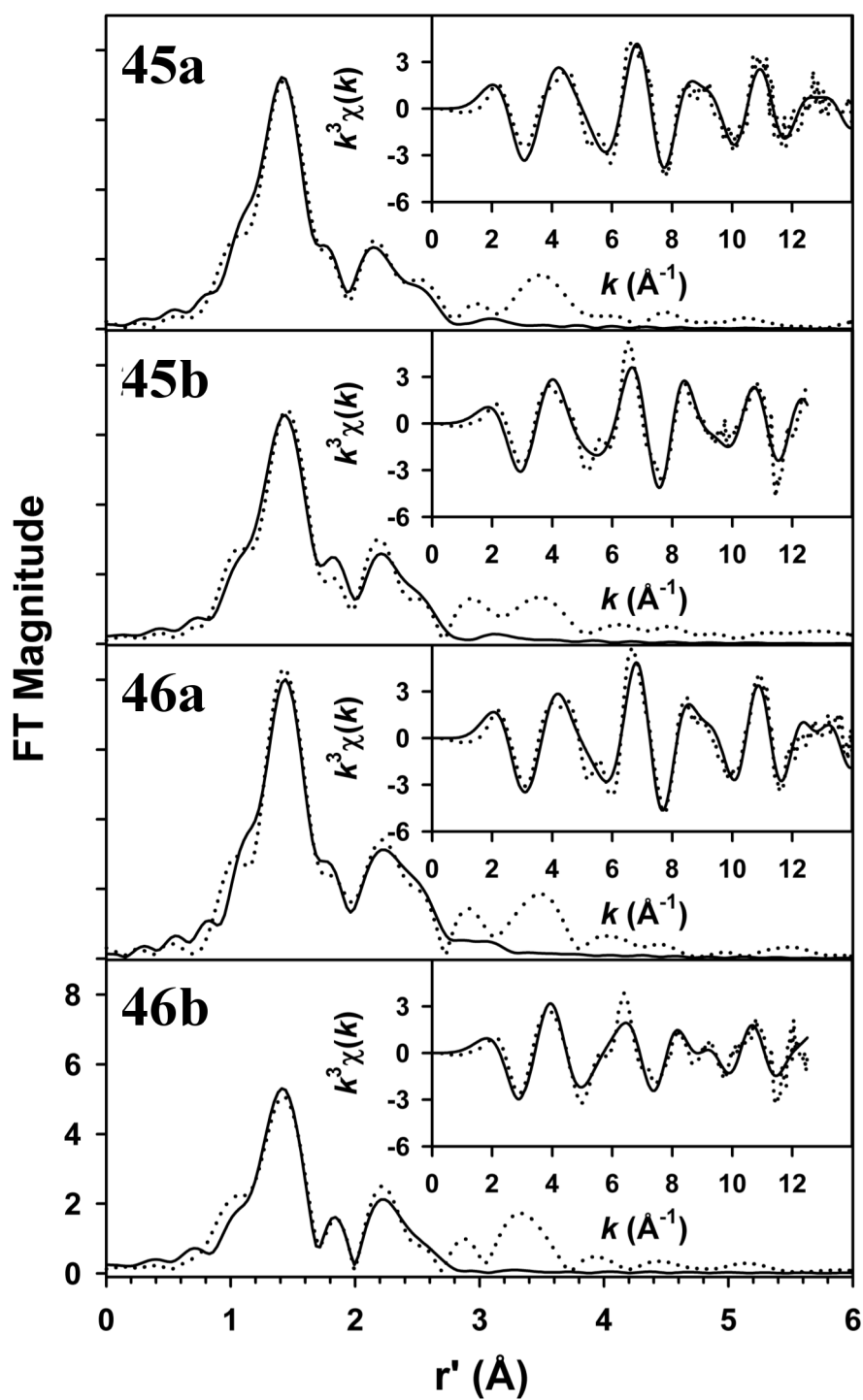


Figure 3.8. Representative best fits to k^3 -weighted EXAFS data of **45a**, **45b**, **46a**, and **46b**. Experimental data is shown as a dotted line, while the best fit is shown as a solid line.

Fascinatingly, dramatic differences in the ligand-binding mode are predicted whether the unpaired electron resides in a d_{xz} - or d_{z^2} -like orbital, where the ligands are coordinated either in monodentate (d_{xz}) or bidentate (d_{z^2}) fashion (figs. A.52 to A.54). The metal-ligand bond-length predictions are also predicted to be affected by the nature of the binding mode (table 3.1). Critically, the XAS-determined Ni–O bond length for **46b** correlates well with that predicted for **46b** with the unpaired electron residing in a d_{z^2} -like molecular orbital. The XAS thus suggests that in **46b** the –ONO₂ ligand may be bidentate, whereas for **44b** and **45b** the ancillary ligands are likely monodentate. DFT predicts negligible energy differences between **44-46b** with the respective binding modes, while EPR suggests that for **46b** the d_{z^2} is occupied, and thus all three should have bidentate donors.

Overall, the DFT calculations correlate well with the XAS-determined bond lengths, although the binding mode for the ancillary O-donor ligands remains unclear. Importantly, the –ONO₂ ligand in **46b** appears to be the weakest-field donor, causing **46b** to be the most electrophilic oxidant.

3.4 Oxidative reactivity

3.4.1 Oxidation of O–H bonds

In order to ascertain the effect of varying the oxygen-adduct (*i.e.* –OCO₂H for **44b**, –OAc for **45b**, –ONO₂ for **46b**), the reaction between 2,6-di-*tert*-butylphenol, in excess, and **45b** and **46b** was performed at -40 °C. It was demonstrated in chapter 2 that **44b** reacted with 2,6-DTBP at -40 °C. In order to ensure a fair and effective comparison, magic blue was used as the oxidant in the preparation of **45b** and **46b** (as was the case for **44b**), and the same reaction temperature (-40 °C) and solvent medium (acetone) was used for all three reactivity studies.

The reactions between **45b** and **46b** and 2,6-DTBP were monitored by electronic absorption spectroscopy: upon addition of an excess of substrate (>10 equiv. 2,6-DTBP) to 0.3 mM solutions of **45b** and **46b** in acetone, decay of the absorbance features attributed to **45b** and **46b** was observed. After the reactions, the radical homo-coupling product 3,3',5,5'-tetra-*tert*-butyl-[1,1'-bis(cyclohexane)]-2,2',5,5'-tetraene-4,4'-dione, together with small amounts of its hydroquinoid form 3,3',5,5'-tetra-*tert*-butyl-[1,1'-biphenyl]-4,4'-diol (Scheme sch. A.1), were detected by ESI MS.

The decay was monitored over the course of the reaction, and pseudo first order rate constants (k_{obs}) were obtained by exponential fitting of the decay plot. Second-order rate

constants (k_2) were determined by plotting k_{obs} (determined at varying substrate concentrations) against substrate concentration and calculating the slope of the resulting linear plot (fig. 3.9). The reactions of **45b** and **46b** with 2,6-DTBP proceeded with k_2 of 0.125 and 1.96 $\text{M}^{-1} \text{s}^{-1}$, respectively (table 3.5). The k_2 determined for **45b** was thus comparable with that measured for **44b** ($k_2 = 0.104 \text{ M}^{-1} \text{s}^{-1}$), while that determined for **46b** was approximately 15 times greater. The $-\text{ONO}_2$ ligand thus appears to enhance the oxidative reactivity of **46b** by an order of magnitude compared to the terminal $-\text{OCO}_2\text{H}$ and $-\text{OAc}$ ligands in **44b** and **45b**.

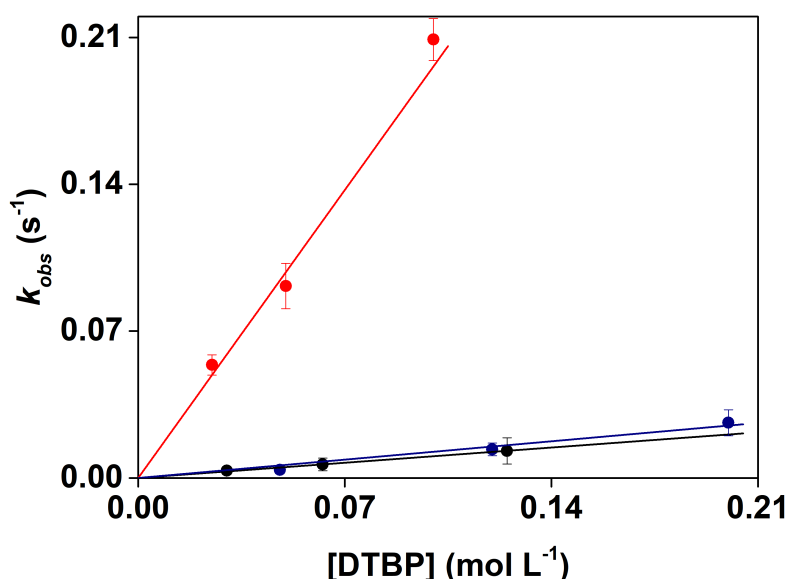


Figure 3.9. Plots of k_{obs} versus [2,6-DTBP] determined for the reaction between **44b** (black), **45b** (blue), and **46b** (red) and 2,6-DTBP at $-40\text{ }^{\circ}\text{C}$ in acetone.

k_2 was also determined for the reaction of **46b** with 2,4-di-*tert*-butylphenol (2,4-DTBP, $k_2 = 158 \text{ M}^{-1} \text{s}^{-1}$), which was 80 times larger than that of 2,6-DTBP (fig. 3.10). Importantly, different reaction kinetics between these two sterically disparate substrates by the same oxidant has been considered to imply a HAT mechanism.¹⁸ Furthermore, a kinetic isotope effect for the reaction of **44b** with 2,6-DTBP of 2.1 was previously measured (chapter 2). These rate constants and KIE values are a strong indication that **44-46b** perform HAT/CPET, rather than a stepwise form of proton coupled electron transfer on phenols.

Mayer and co-workers have been to the fore in defining the HAT reactivity properties of metal-based oxidants.^{19–21} They have demonstrated that thermodynamic driving forces (ΔG° of the HAT reaction) determine the reactivity properties of metal-based oxidants. In

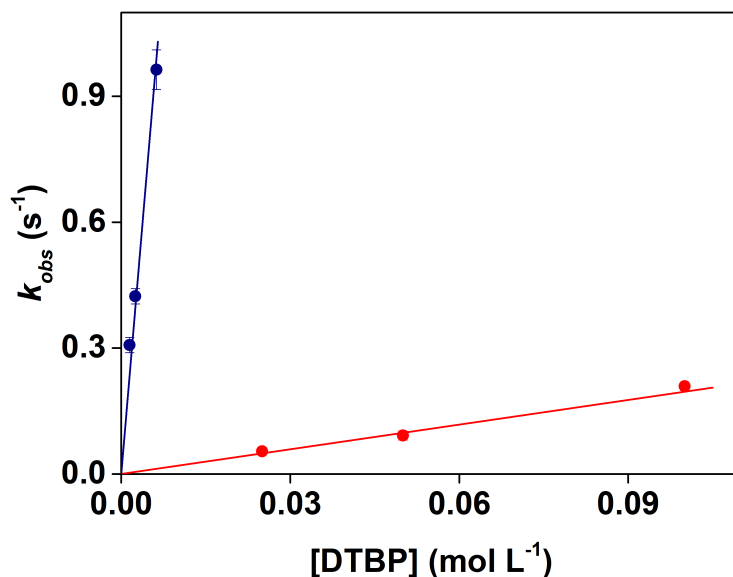


Figure 3.10. Plots of k_{obs} versus [DTBP] determined for the reaction between **46b** and 2,4-DTBP (blue), and for the reaction between **46b** and 2,6-DTBP (red), at -40 °C in acetone.

the HAT reactions between **44-46b** and 2,6-DTBP, ΔG° would explicitly be correlated to the BDFE of the newly formed O–H bond in the $[\text{Ni}^{\text{II}}(\text{O}(\text{H})\text{X})(\text{pyN}_2^{\text{Me}_2})]$ products (defined as **44-46a(H)**). The $\text{BDFE}_{\text{O-H}}$ can be defined as the sum of the free energies of two steps (plus a constant), $[\text{Ni}^{\text{III}}(\text{OX})(\text{pyN}_2^{\text{Me}_2})]$ (**44-46b**) + $e^- \rightarrow [\text{Ni}^{\text{II}}(\text{OX})(\text{pyN}_2^{\text{Me}_2})]^-$ (**44-46a**) and $[\text{Ni}^{\text{II}}(\text{OX})(\text{pyN}_2^{\text{Me}_2})]^-$ (**44-46a**) + $\text{H}^+ \rightarrow [\text{Ni}^{\text{II}}(\text{O}(\text{H})\text{X})(\text{pyN}_2^{\text{Me}_2})]$ (**44-46a(H)**), which are represented by $E_{\text{Ni}^{\text{II}}/\text{Ni}^{\text{III}}}^0$ of **44-46a** and the $\text{p}K_{\text{aO-H}}$ of **44-46a(H)**, respectively.

Attempts were carried out to calculate the $\text{BDFE}_{\text{O-H}}$ for **44-46a(H)** by obtaining $E_{\text{Ni}^{\text{II}}/\text{Ni}^{\text{III}}}^0$ for **44-46a** and a $\text{p}K_{\text{aO-H}}$ for **44-46a(H)**. Cyclic voltammograms for solutions of **44-46a** in acetone (0.1 M Bu_4NPF_6 , scan rate of 0.05 Vs^{-1}) displayed quasi-reversible ($E_{\text{pa,pc}}$: **44a**: 0.11 V; **45a**: 0.07 V; **46a**: 0.13 V) redox waves at $E_{1/2} = 0.48, 0.35$, and 0.56 V vs. Fc^+/Fc respectively (fig. 3.11). The measured $E_{\text{Ni}^{\text{II}}/\text{Ni}^{\text{III}}}^0$ for **44-46a** showed the expected correlation with the electronic properties of the terminal ligands, *i.e.* the more basic ligands yielded complexes with smaller $E_{\text{Ni}^{\text{II}}/\text{Ni}^{\text{III}}}^0$ ($-\text{OAc} < -\text{OCO}_2\text{H} < -\text{ONO}_2$).

A comparison of the $\text{p}K_{\text{a}}$ of the conjugate acids of the ligands showed that the $-\text{OCO}_2\text{H}$ and $-\text{OAc}$ ligands have similar values (aqueous scale $\text{p}K_{\text{a}}$ of $\text{AcOH} = 4.7$, $\text{H}_2\text{CO}_3 = 3.5$).^{22,23} In contrast the $-\text{ONO}_2$ ligand is much more electron-poor (aqueous scale $\text{p}K_{\text{a}}$ of $\text{HNO}_3 = -1.2$).²⁴ The most electrophilic Ni^{III} -oxygen adduct is therefore likely to be **46b**, based on the $E_{\text{Ni}^{\text{II}}/\text{Ni}^{\text{III}}}^0$ for **46a**.

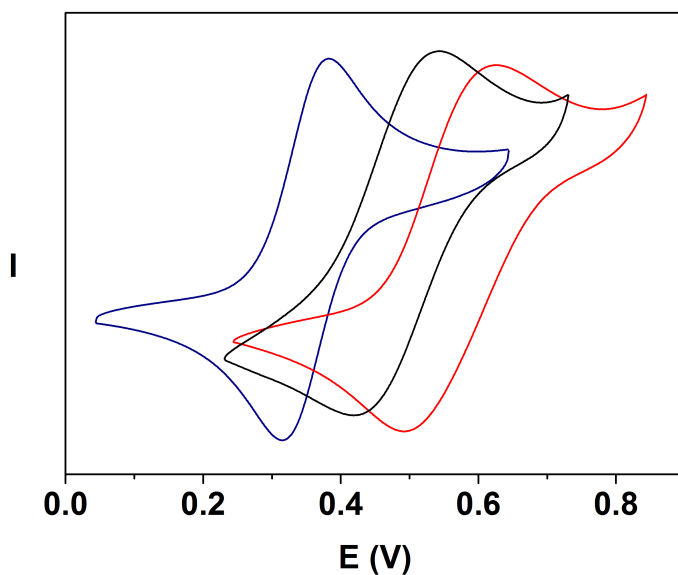


Figure 3.11. Steady state cyclic voltammograms of **44a** (black), **45a** (blue), and **46a** (red), vs. Fc^+/Fc ; conditions: 0.3 mM (acetone), 0.1 M Bu_4NPF_6 , scan rate 0.05 V s^{-1} , room temperature.

Attempted determination of the $\text{p}K_a$ of the O–H in **44-46a(H)**.

It was not possible to synthesise the conjugate acid complexes **44-46a(H)** (that is, $[\text{Ni}^{\text{II}}(\text{H}_2\text{CO}_3)(\text{pyN}_2^{\text{Me}_2})]$, $[\text{Ni}^{\text{II}}(\text{HOAc})(\text{pyN}_2^{\text{Me}_2})]$, $[\text{Ni}^{\text{II}}(\text{HNO}_3)(\text{pyN}_2^{\text{Me}_2})]$). Upon reaction between AcOH or HNO_3 (1 equiv., room temperature) and complex **47**, the complex decomposed to yield $\text{H}_2\text{pyN}_2^{\text{Me}_2}$, as evidenced by ^1H NMR spectroscopy (figs. A.36 and A.37). Similarly, electronic absorption and ^1H NMR analyses of the reaction between **45a** and either $\text{Et}_2\text{O} \cdot \text{HBF}_4$ or AcOH showed protonation and decomposition of the complex (figs. A.38 to A.40). An experimental determination of the $\text{p}K_a$ values of **44-46a(H)** is thus impossible, and in turn the $\text{BDFE}_{\text{O-H}}$ for **44-46a(H)** cannot be calculated.

Discussion on the relative HAT reactivities of **44-46b** towards phenols.

In considering the reaction between **44-46b** and phenols, the following factors were considered:

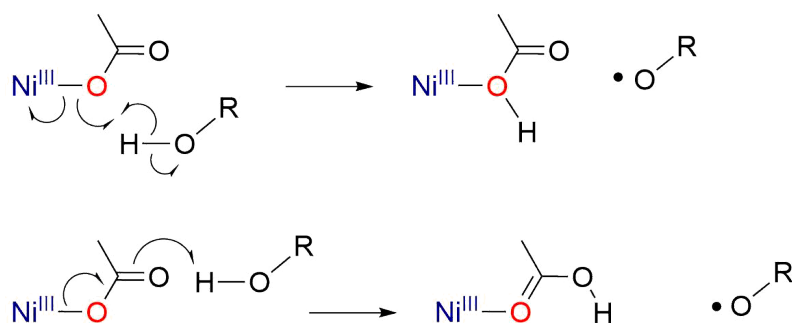
(a) On the ancillary ligands of **44-46b** ($-\text{OCO}_2\text{H}$, $-\text{OAc}$, $-\text{ONO}_2$) there are multiple O-atoms that can be the acceptor/binding site of the incoming H-atom during the reaction between **44-46b** and 2,6-DTBP. It is also possible that rather than the ancillary O-atom donor, it is the carboxamido N or O atoms that accept the proton. Given the stark differences in reactivity of **46b** compared to **44-45b**, it is likely that the H-atom to be delivered

to the ancillary ligand. While the reactivity studies indicated a (concerted) HAT reaction, that does not necessarily mean the proton and electron are delivered to the same location (sch. 3.3). Arguments can be made for at least two mechanistic postulates (thus HAT or separated concerted proton and electron transfer), where the incoming proton either arrives at the proximal or distal O atoms of the metal bound $-\text{OCO}_2\text{H}$, $-\text{OAc}$, and $-\text{ONO}_2$ ligands in **44-46b**.^{25,26}

(b) According to cyclic voltammetry **46a** displayed a higher $E_{\text{Ni}^{II/III}}^0$ than **44-45a**, while XAS indicated that **46b** displayed the longest Ni–O bond length. These observations indicate that the $-\text{ONO}_2$ ligand in **46b** is a relatively weak-field donor, and causes the Ni^{III} –oxygen adduct **46b** to be relatively more electrophilic.

(c) The $\text{BDFE}_{\text{O-H}}$ in **44-46a(H)** could not be determined, preventing an accurate comparison of the relative $\text{BDFE}_{\text{O-H}}$ to relative reactivity. Critically, it cannot be said with certainty that reaction of **44-46a** with H^+ -donors would result in the same O-atom being protonated as reaction of **44-46b** with H-atom donors.

(d) HNO_3 is considerably more acidic than H_2CO_3 and AcOH . Based on this, one can postulate that when comparing metal-bound HNO_3 to metal-bound H_2CO_3 and AcOH in **44-46a(H)**, that the $\text{p}K_a$ of the HNO_3 in **46a(H)** will be lower than for **44-45a(H)**. (e) For free AcOH and HNO_3 the $\text{BDE}_{\text{O-H}}$ are 112 kcal/mol and 101.7 kcal/mol, respectively.²⁷ To the best of my knowledge the $\text{BDE}/\text{BDFE}_{\text{O-H}}$ of H_2CO_3 are yet to be predicted/determined. Based on the higher $\text{BDE}_{\text{O-H}}$ value for AcOH , one would anticipate the acetoxyl radical to display higher rate constants for HAT than the nitrate radical ($\text{NO}_3^\bullet$). This contrasts with the observation that $-\text{ONO}_2$ -ligated **46b** displayed a higher k_2 than $-\text{OAc}$ -ligated **45b**, suggesting that the $\text{BDFE}_{\text{O-H}}$ in **46a(H)** is greater than that in **44a(H)** or **45a(H)**.



Scheme 3.3. Possible PCET mechanisms for the reaction of Ni^{III} -oxygen adducts (Ni^{III} -acetate here) with alcohols (ROH). Top: classical HAT mechanism; Bottom: separated concerted proton and electron transfer.

In summary, **46a** displayed a higher $E_{\text{Ni}^{II/III}}^0$ than **44-46a**, and **46b** is postulated to be the most electrophilic oxidant, while **46a(H)** is postulated to contain a more acidic proton

than **44-45a(H)**. **46b** displayed a higher k_2 for the oxidation of phenols, suggesting that the BDFE_{O-H} in **46a(H)** is greater than that in **44-45a(H)**. Based on these observations, one can surmise that in the reaction between **44-46b** and phenols, electron transfer has a greater contribution to HAT reaction rate than proton transfer. This is because the postulated relatively low pK_a value in **46a(H)** does not cause a relatively low reaction rate, whereas the relatively high $E_{Ni^{II}/III}^0$ for **46a** appears to correlate with a higher oxidation rate for **46b**.

This is an interesting outcome, because it suggests the reactivity of high-valent oxidants may be tuned by simply tuning the electronic properties of the ancillary oxygen-atom donor ligand. Examples of either the effect of the redox potential²⁸ or of basicity²⁹ prevailing have been observed in the literature, although the modifications in the complexes are not as simple as the substitution of a terminal oxygen-ligand.

3.4.2 Oxidation of C–H bonds

At low temperatures (-40 °C), only 1-benzyl-1,4-dihydronicotinamide (BNAH, BDE = 68 kcal/mol) and 10-methyl-9,10-dihydroacridine (BDE = 74 kcal/mol),³⁰ were capable of bringing about the decay of **45b** and **46b** (*i.e.* were oxidized by **45b** and **46b**). The analysis of these reactions is however complicated by the fact that the substrates can act as hydride donors, as well as hydrogen atom donors. At room temperature the reactivity of **45b** towards hydrocarbon substrates with gradually increasing C–H bond strengths (BDE = 78-90 kcal/mol)^{31,32} including xanthene, 9,10-dihydroanthracene (DHA), fluorene, benzyl alcohol, ethylbenzene and toluene was explored.

45b was found to react with all of the listed substrates at 25 °C, along time scales that allowed kinetic analysis of the reactions. k_2 was determined for the reaction of each of these substrates with **45b** using methods analogous to those described above for phenols (table 3.6 and figs. A.41 to A.46 and A.48 to A.50). A plot of the logarithms of the k_2 for the reaction of **45b** with each substrate against the substrate BDE_{C-H} showed a linear correlation (fig. 3.12). This is what was expected for a HAT mechanism, in which BDEs determine the ΔH° of the reaction.* Conversely, the correlations between k_2 and either pK_a or reduction potentials $E_{Ni^{II}/III}^0$ of the substrates are poor: the C–H bond of fluorene is more acidic than that of any of the other substrates, and xanthene is far more easily oxidized than the rest.²¹ The observed linear relationship between reaction rate and BDE_{C-H} is a strong indication of a HAT rate-determining step.

*It should be noted that while the thermodynamic relationships are strictly meant to hold for free energies, it is often necessary to substitute BDEs for BDFEs, due to the limited availability of BDFE data in the literature.

Deriving Gibbs energies of activation from the measured k_2 values, a $\Delta^\ddagger G/\Delta(BDE)$ slope of -0.31 can be determined (fig. A.51). This value compares favourably with the $\Delta^\ddagger G/\Delta G^\circ$ value of -0.5 predicted by Marcus theory,^{19,20,33} and experimental values in the range of -0.15 – -0.7 for other comparable complexes (table 3.2).

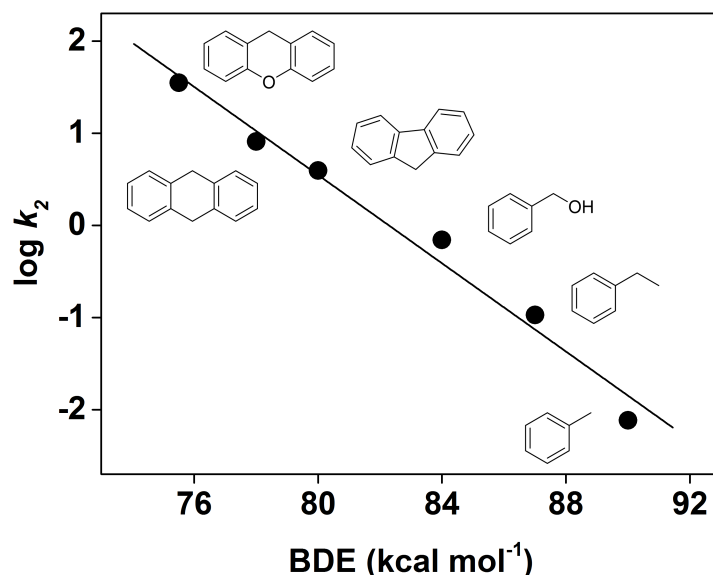


Figure 3.12. Plot of $\log(k_2)$, for the reactions of **45b** with hydrocarbon substrates, measured at 25 °C, against the BDE_{C-H} of the substrates. BDEs from references.^{31,32} The reaction rate of DHA was corrected by a factor of 2 to account for the second HAT event from anthracenyl radical.

Analysis of the post-reaction mixtures was conducted by GC-MS, and the identified oxidized products were consistent with HAT-initiated oxidation. Oxygenated products were formed from all substrates (xanthone from xanthene, anthraquinone from DHA, fluorenone from fluorene, benzoic acid from benzyl alcohol and toluene and acetophenone from ethylbenzene, sch. A.2). However, from the reaction of DHA with **45b**, the main product was the aromatised anthracene, with only traces on anthraquinone being formed. In no case products incorporating chlorine or acetate moieties were found, demonstrating that the NaOCl/AcOH oxidant is not responsible for the substrate oxidation.^{34†}

To further investigate the mechanism of the reaction between **45b** and hydrocarbon substrates, the deuterated substrates $[D_2]$ xanthene and $[D_4]$ DHA were employed. The reac-

[†]The absence of acetate-containing products makes a rebound recombination mechanism unlikely, *i.e.* one in which HAT is followed by reaction of the resulting carbon-based radical with a ligand in the metal coordination sphere. More likely, water or dioxygen in the solution is the source of the oxygen groups in the oxygenated products. When the oxidation of xanthene was performed in the presence of 30 μ L of $H_2^{18}O$, both $[^{16}O]$ xanthone and $[^{18}O]$ xanthone were identified in approximately 1:1 ratio by ESI-MS.

tions with the deuterated substrates proceeded more slowly than with the corresponding protic substrates, giving kinetic isotope effect values of 3.3 and 3.0 respectively (figs. A.41 and A.42). These values closely match the KIE value determined for the reaction between **44b** and 2,6-DTBP (2.1, chapter 2).

The presence of a primary kinetic isotope effect lends further evidence that C–H bond breaking occurs in the rate determining step. The relatively small size of the effect could be explained by the high temperature of the experiment. Should the difference in activation energies be exactly equal to the difference between the zero-point energies of C–H and C–D stretching vibrations, a KIE of 6.9 would be predicted at 25 °C.^{35,36} Lower values, as in the case of **44b** and **45b**, can arise from a not fully linear O···H···C reaction axis, or from a significant vibration involving the hydrogen atom in the transition state.³⁵

DHA is a commonly employed substrate in HAT studies, allowing to compare the reactivity properties of **45b** to those of previously reported high-valent metal-oxygen adducts. The determined k_2 values for the reaction between DHA and selected complexes of Mn, Fe, Ru and Cu at 25 °C (table 3.2) are tabulated. The k_2 for **45b** was about half of that of $[\text{Fe}^{\text{IV}}(\text{O})(\text{N4Py})]^{2+}$, and only one order of magnitude smaller than $[\text{Ru}^{\text{IV}}(\text{O})(\text{bpy})_2(\text{py})]^{2+}$ and $[\text{Cu}^{\text{III}}(\text{OH})(\text{pyN}_2^{i\text{Pr}_2})]$, which rank among the most reactive oxidants reported to date. Permanganate (MnO_4^-), as well as the Mn^{IV} -dioxo $[\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{O})_2]$, are considerably slower. It should be noted that **45b** is not an oxo complex. By comparison, an Fe^{III} -alkoxide complex ($[\text{Fe}^{\text{III}}(\text{OCH}_3)(\text{PY5})]^{2+}$) is a much weaker oxidant compared to $\text{Fe}^{\text{IV}}=\text{O}$. The high reaction rate of **45b**, as well as that of Tolman's $\text{Cu}^{\text{III}}-\text{OH}$ complex, lend weight to the postulated high oxidizing power of complexes based on the late-transition metals.

Table 3.2. Kinetic parameters for the HAT reactions of selected high valent metal-oxo and other metal-oxygen complexes with DHA.

	$k_2^{[\text{a}]} (\text{M}^{-1} \text{s}^{-1})$	KIE ^[b]	$-\Delta G^\ddagger / \Delta(\text{BDE})^{[\text{c}]}$	Reference
45b	8.11	3.0	0.31	
$[\text{Mn}^{\text{VII}}\text{O}_4]^-$	0.12		0.69	37,38
$[\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{O})_2]$	~0.03	3.78 ^[d]	0.21	39
$[\text{Fe}^{\text{IV}}(\text{O})(\text{N4Py})]^{2+}$	18	20 ^[e]	0.15	40,41
$[\text{Fe}^{\text{III}}(\text{OCH}_3)(\text{PY5})]^{2+}$	0.0049	5.5	0.17	42
$[\text{Ru}^{\text{IV}}(\text{O})(\text{bpy})_2(\text{py})]^{2+}$	125	50-100	0.47	31
$[\text{Cu}^{\text{III}}(\text{OH})(\text{pyN}_2^{i\text{Pr}_2})]$	~190	24 ^[f]	0.37	43,44

[a] For the reaction with DHA at 25 °C. For $[\text{Mn}^{\text{IV}}(\text{Me}_2\text{EBC})(\text{O})_2]$ and $[\text{Cu}^{\text{III}}(\text{OH})(\text{pyN}_2^{i\text{Pr}_2})]$, data at 25 °C was not available; values were derived from the experimentally determined activation parameters via the Eyring equation; [b] Kinetic isotope effect for the oxidation of DHA, measured at 25 °C unless otherwise noted; [c] Empirically determined slope of the activation free energy vs. substrate BDE regression line, for a series of hydrocarbon substrates; [d] measured at 288 K; [e] measured at 313 K; [f] measured at 248 K.

3.5 Conclusions

Two new $[\text{Ni}^{\text{III}}(\text{OX})(\text{pyN}_2^{\text{Me}_2})]$ compounds, **45b** and **46b**, were synthesised and fully characterised, demonstrating the high-yield preparation of pure Ni^{III} oxidants. Comparison of their oxidative reactivity towards 2,6-di-*tert*-butylphenol, showed the $-\text{ONO}_2$ complex **46b** reacted 15 times faster than its $-\text{OAc}$ and $-\text{OCO}_2\text{H}$ congeners, indicating that the electron-deficiency of the complex is the prevalent factor in determining oxidizing potency.

For **45b** a linear Polanyi relationship between k_2 and substrate $\text{BDE}_{\text{C-H}}$ provides strong evidence for the postulated HAT mechanism of C–H bond activation. **45b** was capable of reacting with relatively hard to oxidise substrates and has a high reaction rate towards DHA, of the same order of magnitude as $\text{Fe}^{\text{IV}}=\text{O}$ complexes, in spite of the stabilization afforded by substitution at the O-atom (thus carboxylato versus oxo complexes).

This demonstrates the effectiveness of late-transition metal oxidants in the activation of strong C–H bonds, and the ease at which the reactivity of high-valent metal-oxygen adducts can be tuned by simple manipulation of anionic constituents.

3.6 Experimental section

Physical Methods

Electronic absorption spectra were recorded on a Hewlett Packard (Agilent) 8453 diode array spectrophotometer (190-1100 nm range) in quartz cuvettes cooled using a liquid nitrogen cooled cryostat from Unisoku Scientific Instruments (Osaka, Japan). ^1H and ^{13}C NMR analyses were performed on an Agilent MR400 instrument (400.13 MHz for ^1H NMR and 100.61 MHz for ^{13}C NMR). GC-MS was performed using a GCT Premier Micromass time of flight mass spectrometer. Electrospray ionization (ESI) mass spectra were acquired using a Micromass time of flight spectrometer (TOF), interfaced to a Waters 2690 HPLC, or by direct injection in the mass spectrometry instrument. ATR-FTIR spectra were recorded on a Perkin-Elmer Spectrum 100 Fourier transform infrared spectrometer. CHN elemental content analyses were performed on an Exeter Analytical CE 440 elemental analyser fitted with a Varian 55B SpectraAA atomic absorption spectrometer. Electron paramagnetic resonance spectra were recorded on a Magnetechnic Miniscope MS2000 instrument, with liquid nitrogen cooling. Cyclic voltammetry experiments were conducted with a CH Instruments 600E electrochemical analyser, using a glassy carbon working electrode, a platinum wire counter electrode and an Ag/AgNO₃ 0.01 M reference electrode.

Materials and synthesis

Reactions with air-sensitive materials were conducted under an inert atmosphere using standard Schlenk techniques or in a nitrogen atmosphere glove-box. All solvents and reagents were purchased from commercial sources and used as received, unless otherwise stated. Anhydrous CH₃CN, CH₂Cl₂, and diethylether were dispensed through an Innovative Technology PureSolv EN solvent purification system and deoxygenated by sparging with argon. Anhydrous acetone was obtained by drying over magnesium sulfate, then over 4 Å molecular sieves, distilling and deoxygenating by sparging with argon. NaOCl was purchased as 17% active chlorine (2.4 M) solution and stored frozen until use. Fluorene was recrystallized from hexanes; 2,4-di-*tert*-butylphenol and 2,6-di-*tert*-butylphenol were recrystallized from ethanol. *N,N'*-(2,6-dimethylphenyl)pyridine-2,6-dicarboxamide,² [Ni^{II}(OCO₂H)(pyN₂^{Me₂})]Et₄N (**44a**),² [D₂]xanthene,⁴⁵ [D₄]9,10-dihydroanthracene⁴⁵ and 10-methyl-9,10-dihydroacridine⁴⁶ were prepared according to reported procedures. Crude Et₄NNO₃ was prepared by the reaction of Et₄NOH and HNO₃ in methanol, followed by precipitation with excess acetone.

Synthesis of $[\text{Ni}^{\text{II}}(\text{CH}_3\text{CN})(\text{pyN}_2^{\text{Me}_2})]$, acetonitrile(*N,N'*-bis(2,6-dimethylphenyl)-2,6-pyridinedicarboxamido)nickel(II), 47 - method A

The reaction was conducted under an inert (N_2) atmosphere. *N,N'*-(2,6-dimethylphenyl)-pyridine-2,6-dicarboxamide (0.550 g, 1.47 mmol) was dissolved in anhydrous CH_3CN (15 mL). Addition of NaH (60% dispersion in mineral oil, 0.118 g, 2.95 mmol, 2 eq.) resulted in immediate gas evolution and caused the solution to turn yellow and some precipitate to form. When bubbling ceased, $\text{Ni}(\text{OTf})_2$ (0.570 mg, 1.6 mmol, 1.1 eq.) was added. The resulting red mixture was stirred for 3 h at room temperature, after which the solvent was removed *in vacuo*; the residues were taken up in anhydrous CH_2Cl_2 (60 mL), filtered and evaporated to yield the product as a red-brown powder (0.310 mg, 0.66 mmol, 45%). Crystals suitable for X-ray diffraction were obtained by diffusion of Et_2O into a concentrated CH_2Cl_2 solution.

δH (400 MHz, CDCl_3): 8.07 (1H, t, $J = 7.7$ Hz, 4-py), 7.75 (2H, d, $J = 7.7$ Hz, 3,5-py), 6.99–6.81 (6H, m, ArH), 2.49 (12H, s, ArCH₃), 1.28 (3H, s, CH_3CN).

δC (101 MHz, CDCl_3): 166.0 (NC=O), 151.0 (pyridine CH), 144.1 (aniline Cq), 141.3 (pyridine Cq), 134.0 (aniline Cq), 127.5 (aniline CH), 125.0 (aniline CH), 123.5 (pyridine CH), 122.4 (CH_3CN), 19.0 (ArCH₃), 1.1 (CH_3CN).

ESI-MS (m/z): Found: 471.1331 ($[\text{M} + \text{H}]^+$, $\text{C}_{25}\text{H}_{25}\text{N}_4\text{O}_2\text{Ni}$ requires 471.1331).

Anal. Calcd. for $\text{C}_{25}\text{H}_{24}\text{N}_4\text{NiO}_2$: C, 63.73; H, 5.13; N, 11.89. Found: C, 62.89; H, 5.12; N, 11.75.

ν_{max} (ATR-FTIR) / cm^{-1} : 2974 (CH), 2944 (CH), 2913 (CH), 2337w ($\text{C}\equiv\text{N}$), 2311w ($\text{C}\equiv\text{N}$), 1630s, 1585, 1466, 1362s, 830, 757s, 675s.

λ_{max} /nm: (CH_3CN) 245 (ϵ / $\text{M}^{-1} \text{cm}^{-1}$ 19500), 340 (11000), 435 (1400), 560sh (110).

Synthesis of $[\text{Ni}^{\text{II}}(\text{CH}_3\text{CN})(\text{pyN}_2^{\text{Me}_2})]$, acetonitrile(*N,N'*-bis(2,6-dimethylphenyl)-2,6-pyridinedicarboxamido)-nickel(II), 47 - method B

Anhydrous NiCl_2 (0.200 g, 1.54 mmol) was refluxed in CH_3OH (20 mL) until complete dissolution. The resulting pale green solution was cooled down to room temperature, and *N,N'*-bis(2,6-dimethylphenyl)pyridine-2,6-dicarboxamide (0.576 g, 1.54 mmol, 1 eq.), was added, followed by NaOCH_3 (prepared by dissolving 0.074 g of sodium, 3.22 mmol, 2.1 eq., in 5 mL CH_3OH). A dark red mixture resulted. The mixture was refluxed for 1 h, then the methanol was removed by evaporation; the solid was taken up in CH_3CN (40 mL), and heated to reflux for 12 h. The solvent was removed again, the solid taken up in CH_2Cl_2 (100 mL), dried over MgSO_4 and filtered. Removal of the solvent yielded the product as a red-brown powder (540 mg, 1.15 mmol, 74%).

Synthesis of [Ni^{II}(OAc)(pyN₂^{Me₂)]Et₄N, tetraethylammonium acetato(*N,N'*-bis(2,6-dimethylphenyl)-2,6-pyridinedicarboxamido)nickelate(II), 45a}

47 (0.204 g, 0.43 mmol) was dissolved in CH₃CN (3 mL). Et₄NOAc (0.090 g, 0.48 mmol, 1.1 eq.) was subsequently added and the solution stirred for 10 minutes. Stirring was ceased and Et₂O (20 mL) was layered on top of the solution. Over the course of 5 days, bright red crystals of the product formed, and were recovered by decanting of the solution (0.160 g, 0.25 mmol, 58%). Crystals suitable for X-ray diffraction were identified in the product.

δ H (400 MHz, CDCl₃): 7.86 (1H, t, *J* = 7.7 Hz, 4-py), 7.52 (2H, d, *J* = 7.7 Hz, 3,5-py), 6.93–6.62 (6H, m, Ar*H*), 2.88 (8H, m, NCH₂CH₃), 2.57 (12H, s, ArCH₃), 1.09 (12H, m, NCH₂CH₃), 0.78 (3H, s, CH₃CO₂).

δ C (101 MHz, CDCl₃): 176.7 (CH₃C=O), 165.4 (NC=O), 152.3 (pyridine CH), 144.5 (aniline *Cq*), 138.4 (pyridine *Cq*), 134.8 (aniline *Cq*), 126.8 (aniline CH), 123.5 (aniline CH), 121.7 (pyridine CH), 52.0 (NCH₂CH₃), 22.1 (CH₃CO₂), 19.4 (ArCH₃), 7.4 (NCH₂CH₃).

ESI-MS (*m/z*): Found: -488.1128 ([Ni(OAc)(pyN₂^{Me₂)]⁻, C₂₅H₂₄N₃O₃Ni requires 488.1120).}

Anal. Calcd. for C₃₃H₄₄N₄NiO₄·H₂O: C, 62.18; H, 7.27; N, 8.79. Found: C, 62.47; H, 7.17; N, 8.82.

ν_{max} (ATR-FTIR) /cm⁻¹: 2971 (CH), 2946 (CH), 2912 (CH), 1620s, 1608, 1585, 1474, 1430, 1370s, 996, 768s, 680s.

λ_{max} /nm: (CH₃CN) 245 (ϵ /M⁻¹ cm⁻¹ 20000), 295sh (9800) 385 (7000), 470sh (1200); (acetone) 390 (6700), 470sh (1200).

Synthesis of [Ni^{II}(ONO₂)(pyN₂^{Me₂)]Et₄N, tetraethylammonium nitrato(*N,N'*-bis(2,6-dimethylphenyl)-2,6-pyridinedicarboxamido)nickelate(II), 46a}

47 (0.230 g, 0.48 mmol) was dissolved in CH₃OH (3 mL). Et₄NNO₃ (0.103 g, 0.54 mmol, 1.1 eq.) was subsequently added and the solution stirred for 10 minutes. Stirring was ceased and Et₂O (20 mL) was layered on top of the solution. Over the course of 4 days, bright red crystals of the product formed, and were recovered by decanting off the solution (0.135 g, 0.22 mmol, 44%). Crystals suitable for X-ray diffraction were identified in the product.

δ H (400 MHz, CD₃OD): 8.24 (1H, t, *J* = 7.5 Hz, 4-py), 7.71 (2H, d, *J* = 7.5 Hz, 3,5-py), 6.97 (6H, br, Ar*H*), 3.33 (8H, m, NCH₂CH₃, overlaps with residual CH₃OH signal), 2.57 (12H, s, ArCH₃), 1.30 (12H, m, NCH₂CH₃).

δ C (101 MHz, CD₃OD): 167.4 (NC=O), 152.8 (aniline C_q), 143.3 (pyridine CH), 128.7 (aniline CH), 126.3 (aniline CH), 124.2 (pyridine CH), 53.2 (NCH₂CH₃), 19.1 (ArCH₃), 7.5 (NCH₂CH₃).

ESI-MS (*m/z*): Found: -491.0870 ([Ni(ONO₂)(pyN₂^{Me₂})]⁻, C₂₃H₂₁N₄NiO₅ requires 491.0871).

Anal. Calcd. for C₃₁H₄₁N₅NiO₅·CH₃OH: C, 58.73; H, 6.93; N, 10.70. Found: C, 58.88; H, 6.77; N, 10.86.

ν_{max} (ATR-FTIR) /cm⁻¹: 2971 (CH), 2946 (CH), 2915 (CH) 1623s, 1609s, 1585, 1471, 1370s, 1290s (NO₃ symm. stretch), 1010, 769, 691, 680.

λ_{max} /nm: (acetone) 340 (ϵ /M⁻¹ cm⁻¹ 9000), 455 (1200).

Preparation of [Ni^{III}(OAc)(pyN₂^{Me₂})], acetato(*N,N'*-bis(2,6-dimethylphenyl)-2,6-pyridinedicarboxamido)nickel(III), **45b or [Ni^{III}(ONO₂)(pyN₂^{Me₂})], nitrato(*N,N'*-bis(2,6-dimethylphenyl)-2,6-pyridinedicarboxamido)nickel(III), **46b** – method A (magic blue)**

2 mL of a 0.3 mM acetone solution of **45a** (for the preparation of **45b**), or **46a** (for the preparation of **46b**), were cooled to the desired temperature (-80 °C < *T* < -40 °C) in a cuvette. 40 μ L of a freshly prepared 15 mM solution of tris(4-bromophenyl)ammoniumyl hexachloroantimonate (magic blue) in acetonitrile were added under continuous stirring. The formation of the Ni^{III} intermediate was immediate as evidenced by the formation of electronic absorption bands at 510 and 760 nm (for **45b**) or 560 and 890 nm (for **46b**).

Preparation of [Ni^{III}(OAc)(pyN₂^{Me₂})], acetato(*N,N'*-bis(2,6-dimethylphenyl)-2,6-pyridinedicarboxamido)nickel(III), **45b – method B (NaOCl/AcOH)**

A solution of **45a** (2 mL, 0.3 mM in acetone) was cooled to the desired temperature (-80 °C < *T* < 25 °C). 6 μ L of a solution of hypochlorous acid (prepared by mixing 0.1 mL acetic acid (1.75 mmol) and 1 mL of 17% NaOCl (2.1 mmol, 1.2 eq.) were added, causing the formation of dark purple **45b**. The characteristic electronic absorption bands of **45b** (λ_{max} = 510 and 760 nm) grew to their maximum intensity in ~5s (at 25 °C), indicating completion of the reaction.

Preparation of [Ni^{III}(ONO₂)(L)], nitrato(*N,N'*-bis(2,6-dimethylphenyl)-2,6-pyridinedicarboxamido)nickel(III), **46b – method B (cerium ammonium nitrate)**

A solution of **46a** (2 mL, 0.3 mM in anhydrous acetone) was cooled to the desired temperature (-80 °C < *T* < -40 °C) in a cuvette. 12 μ L of a CH₃OH solution of (NH₄)₂[Ce^{IV}(NO₃)₆]

(0.25 M) were added under continuous stirring. The characteristic bands of **46b** (λ_{max} = 560 and 790 nm) reached their maximum intensity after 30 s, at -40 °C.

X-Ray diffraction methods

Single crystal X-ray data were collected at 100(2) K on a Bruker Apex II CCD diffractometer using graphite-monochromated Mo-K α radiation (λ = 0.71073 Å), an Oxford Cryo-systems Cobra low temperature device and a MiTeGen micromount. Bruker APEX⁴⁷ software was used to correct for Lorentz and polarization effects. The structures were solved and refined using the Bruker SHELXTL Software Package.^{48,49}

X-ray structure refinements

45a was found to co-crystallise with one molecule of water. Disorder in the dimethylphenyl groups, due to rotation along the Ar-N bond, was modelled using restraints and constraints (SADI, SAME and EADP); occupancy was refined to 70:30%. Hydrogen atoms on the solvent water molecule were located and refined using restraints (DFIX) and constraints (AFIX). The model was refined to convergence. The structure of **46a** contained partially occupied solvent sites which could not be refined; **47** presented no disorder or solvent molecules.

Table 3.3. Selected bond distances (Å) and angles (°) for **44a** (reference²), **45a**, **46a**, and **47**.

	44a	45a	46a	47
Ni–N _{pyridine}	1.817(4)	1.816(1)	1.816(3)	1.813(2)
Ni–N _{amide}	1.895(4)	1.906(2)	1.897(3)	1.889(2)
Ni–OX	1.871(4)	1.870(1)	1.888(2)	
Ni–N _{CH₃CN}				1.855(2)
N _{pyridine} –Ni–N _{amide}	83.40(9)	83.0(1)	83.4(5)	83.6(1)
N _{amide} –Ni–O(/N _{CH₃CN})	96.60(9)	97.1(16)	96.6(4)	96.5(3)
N _{amide} –Ni–N _{amide'}	166.79(18)	165.33(7)	166.66(12)	166.98(8)
N _{pyridine} –Ni–O(/N _{CH₃CN})	178.99(17)	176.66(6)	176.46(16)	179.33(8)

Table 3.4. Crystal data and structure refinement parameters for **45a**, **46a**, and **47**.

	45a	46a	47
Empirical formula	C ₃₃ H ₄₆ N ₄ NiO ₅	C ₃₁ H ₄₁ N ₅ NiO ₅	C ₂₅ H ₂₄ N ₄ NiO ₂
Formula weight	637.45	622.40	471.19
Temperature	100(2) K	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P2 ₁ /c	Cc	P2 ₁ /c
Unit cell dimensions	<i>a</i> = 9.2236(3) Å <i>α</i> = 90° <i>b</i> = 12.0067(4) Å <i>β</i> = 95.7501(9)° <i>c</i> = 29.5763(11) Å <i>γ</i> = 90°	<i>a</i> = 17.8415(9) Å <i>α</i> = 90° <i>b</i> = 11.2027(6) Å <i>β</i> = 109.1470(10)° <i>c</i> = 17.1224(8) Å <i>γ</i> = 90°	<i>a</i> = 13.9373(10) Å <i>α</i> = 90° <i>b</i> = 11.6859(8) Å <i>β</i> = 101.5569(17)° <i>c</i> = 14.2687(9) Å <i>γ</i> = 90°
Volume	3258.95(19) Å ³	3233.0(3) Å ³	2276.8(3) Å ³
Z	4	4	4
Density (calculated)	1.299 Mg/m ³	1.279 Mg/m ³	1.375 Mg/m ³
Absorption coefficient	0.641 mm ⁻¹	0.645 mm ⁻¹	0.881 mm ⁻¹
F(000)	1360	1320	984
Crystal size	0.27 x 0.10 x 0.04 mm ³	0.20 x 0.15 x 0.15 mm ³	0.22 x 0.13 x 0.11 mm ³
Theta range for data collection	1.832 to 27.493°	2.183 to 33.226°	2.874 to 27.999°
Index ranges	-11 ≤ <i>h</i> ≤ 9, -15 ≤ <i>k</i> ≤ 15, -38 ≤ <i>l</i> ≤ 38	-27 ≤ <i>h</i> ≤ 27, -17 ≤ <i>k</i> ≤ 17, -26 ≤ <i>l</i> ≤ 26	-18 ≤ <i>h</i> ≤ 18, -13 ≤ <i>k</i> ≤ 15, -18 ≤ <i>l</i> ≤ 13
Reflections collected	50097	55443	12948
Independent reflections	7466 [R(int) = 0.0387]	12180 [R(int) = 0.0238]	5454 [R(int) = 0.0433]
Completeness to theta=	25.242° 100.0 %	26.000° 100.0 %	26.000° 99.6 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6970	0.7465 and 0.6940	0.7456 and 0.6992
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	7466 / 21 / 389	12180 / 32 / 368	5454 / 0 / 294
Goodness-of-fit on F ²	1.068	1.037	1.023
Final R indices [<i>I</i> > 2σ(<i>I</i>)]	R1 = 0.0362, wR2 = 0.0821	R1 = 0.0555, wR2 = 0.1351	R1 = 0.0384, wR2 = 0.0760
R indices (all data)	R1 = 0.0503, wR2 = 0.0880	R1 = 0.0610, wR2 = 0.1389	R1 = 0.0720, wR2 = 0.0873
Largest diff. peak and hole	0.440 and -0.497 e Å ⁻³	1.368 and -0.997 e Å ⁻³	0.334 and -0.422 e Å ⁻³

Cyclic voltammetry

CV experiments were conducted on 3 mM solutions of compounds **44-46a** in acetone, at room temperature, with a 0.05 V s⁻¹ scan rate. The supporting electrolyte was 0.1 M Bu₄NPF₆. Potentials were referenced to the Fc⁺/Fc couple by addition of an internal ferrocene standard to the solutions of **44-46a**. **45a** and **46a** were measured in air. While the voltammogram of **44a** displayed a redox event even in air, performing the CV under a CO₂ atmosphere improved both reversibility and signal intensity.

EPR Spectroscopy

EPR samples were prepared by freezing solutions of **45b** or **46b** in EPR tubes, prepared according to the above procedures, in liquid nitrogen. The EPR spectra were recorded at 77 K, 9.379 GHz, 31.6 W microwave power, with a 300 mT field sweep in 60 s, and 0.5 mT field modulation amplitude. Integration, simulation, and fitting were executed with Matlab and the easySpin computational package.⁵⁰ Quantification of the concentration of spins in the samples was obtained by comparison of the double integral of the signals to that of a frozen 0.4 mM acetone solution of TEMPO, measured under the same conditions. The concentrations thus determined, together with the electronic absorption spectroscopy absorbance values for the same samples, were used to calculate the absorptivities of **45b** and **46b** via the Beer-Lambert law. The systems were modelled as S = ½ electron spins with axial g tensor with inhomogeneous line broadening (See figs. A.24 to A.26).

Mass spectrometry

Samples for ESI-MS analysis were prepared in the same way (but **45-46b** were frozen in glass vials), and directly injected in the spectrometer immediately after thawing. A desolvation temperature of 100 °C was used.

X-Ray absorption spectroscopy

Samples for X-ray absorption spectroscopy analysis were prepared by transferring solutions of **45a** (50 mM, acetonitrile), **46a** (27 mM, acetone), **45b** (8.5 mM, acetone) and **46b** (3.6 mM, acetone), into XAS sample cups pre-cooled in a liquid nitrogen bath and immediately freezing them. The solution of **45b** was prepared according to method B above, at -45 °C and with initial concentration of the Ni^{II} complex scaled up to 8.5 mM; the solution

of **46b** was prepared according to method B above, at -45 °C and with initial concentration of the Ni^{II} complex scaled up to 4 mM. Acetonitrile was used for **45a** because it allowed for much greater solubility.

X-ray absorption spectroscopy data was collected at beamline 2-2 of the Stanford Synchrotron Radiation Lightsource (SLAC National Accelerator Lab, Menlo Park, CA, USA), with the storage ring operating at 3.0 GeV and 500 mA. A Si(111) double crystal monochromator was used for energy selection, and was detuned by ~30% for higher harmonic rejection. Sample temperatures were maintained at approximately 20 K using a He Displex cryostat. A metallic nickel foil spectrum was recorded simultaneously using a photodiode for internal energy calibration, with the first inflection point of the reference foil edge set to 8333.0 eV. XAS data were collected as fluorescence spectra using a 13 element solid state germanium detector (Canberra), with the following parameters: 10 eV steps/1 second integration time in the pre-edge region, 0.3 eV steps /2 second integration time in the edge, and 0.05k steps in the EXAFS, with integration time increasing in a k^2 -weighted fashion from 2 to 8 seconds over the energy range ($k_{max} = 14k$).

The total detector counts were typically 5-40 kHz, well within the linear range of the detector electronics. Samples were monitored for photoreduction during data collection, however no photoreduction was observed for any sample based on the absence of any scan-to-scan red-shift in the absorption edge. Tandem Mossbauer/XAS cups with a sample window of 4 mm x 10 mm were used as sample cells. Averaging and normalization of the XAS data was performed using Athena.⁵¹

Edge energies were determined as the half-height of the white-line intensity. EXAFS analysis was carried out using Artemis, which incorporates the IFEFFIT fitting engine and FEFF6 for *ab initio* EXAFS phase and amplitude parameters.⁵¹ Crystal structures (either as-is or modified slightly to test different structural models) were used for FEFF6 input to identify significant paths. Fits of **45b** and **46b** were performed on two different models having either monodentate- or bidentate-bound exogenous anions. **45b** was best modelled with a monodentate acetate moiety, while **46b** was best fit using a bidentate nitrate anion. For a given shell in all simulations, the coordination number n was fixed, while r and σ^2 were allowed to float. The amplitude reduction factor S_0^2 was fixed at 0.9, while the edge shift parameter ΔE_0 was allowed to float at a single common value for all shells. The fit was evaluated in k^3 -weighted R-space, and fit quality was judged by the reported R-factor and reduced χ^2 .

Reactivity studies

General procedure for reactivity experiments Solutions of **45b** and **46b** were prepared according to method A (magic blue as oxidant, page 83), at -40 °C, for the reactivity studies with phenols. For hydrocarbon oxidation reactions at room temperature, a solution of **45b** was prepared according to method B (HOCl as oxidant, page 83), the precipitate quickly separated by decanting, and the solution transferred to a cuvette. Substrates were added under stirring as concentrated acetone solutions, or as a neat liquid (benzyl alcohol). For reactions with ethylbenzene and toluene, a substrate/acetone mixture (from 5% to 50%) was used as the solvent. The consumption of **45b** or **46b** was monitored using electronic absorption spectroscopy, by observing the disappearance of the visible/NIR features (**45b**: λ_{max} = 510 and 760 nm **46b**: λ_{max} = 560 and 790 nm) over time. The post-reaction mixtures were diluted with acetone for GC-MS or ESI MS analysis.

Rate constants determination For rate constant determinations a minimum of 10 equivalents of substrate were used to ensure pseudo-first order conditions. The second-order rate constants (k_2) were determined from the linear dependence of the pseudo-first order constants (k_{obs}) on substrate concentration. Values for the observed k_{obs} were obtained by fitting the decay of the absorbance at 510 nm (**45b**) or 560 nm (**46b**) as an exponential. Each experiment was repeated three times, and the average k_{obs} value was utilized for the determination of k_2 .

Table 3.5. Second order rate constants (k_2) for the reactions of **44b**, **45b** and **46b** with phenol substrates at -40 °C (2,4- and 2,6-DTBP).

	Substrate	k_2 (M ⁻¹ s ⁻¹)
44b	2,6-DTBP	0.104
45b	2,6-DTBP	0.125
46b	2,6-DTBP	1.96
46b	2,4-DTBP	158.5

Attempted determination of the pK_a of O–H in **44-46a**(H).

Determining the pK_a values for the conjugate acids of **44-46a** was attempted using electronic absorption spectroscopy, by monitoring the reaction between **44-46a** and various acids, and determining the acid dissociation constant. The following issues presented in

Table 3.6. Second order rate constants (k_2) for the reactions of **45b** with hydrocarbon substrates at 25 °C. a) The reaction rate constant was corrected by a factor of 2 to account for the second HAA event from anthracenyl radical.

Substrate	k_2 ($\text{M}^{-1} \text{s}^{-1}$)	BDE (kcal/mol)
Xanthene	35.1	75.5 ³¹
[D ₂]Xanthene	10.8	
DHA ^[a]	8.11	78 ³¹
[D ₄]DHA ^[a]	2.67	
Fluorene	3.94	80 ³¹
Benzylalcohol	0.692	84 ³²
Ethylbenzene	01.6	87 ³¹
Toluene	0.0076	90 ³¹

considering this experiment: the formed metal-bound AcOH, H₂CO₃, and HNO₃ ligands in **44-46a(H)** are likely to be extremely labile and easily displaced by ligating solvent (acetone, present in large excess). Furthermore, carbonic acid in **44a(H)** is likely to decay to yield CO₂ and H₂O. The spectroscopic properties of **44-46a(H)** are not known, because they could be synthesised independently, thus preventing from differentiating between **44-46a(H)** and solvent substituted adducts thereof. Furthermore, in attempting to determine the pK_a of the O–H group in **44-46a(H)**, it cannot be said with certainty that reaction of **44-46a** with H⁺-donors would result in the same O-atom being protonated as reaction of **44-46b** with H-atom donors.

Nonetheless, the reaction between **45a** and strong acids was explored. Electronic absorption analysis of the reaction between **45a** and Et₂O · HBF₄ or AcOH (2 equiv.) showed that both acids reacted with the Ni^{II} complex at room temperature (figs. A.38 and A.39). Unfortunately, the electronic absorption spectra obtained from these acid/base reactions were not typical of [Ni^{II}(L)] complexes, where one typically expects features in the region λ_{max} = 380–410 nm. This can be attributed to the protonation of the 2,6-pyridinedicarboxamidate ligand rather than the ancillary O-ligand.

Importantly, in ¹H NMR experiments on the reaction between **45a** and Et₂O · HBF₄ addition of even sub-stoichiometric amounts of Et₂O · HBF₄ showed the formation of free *N,N'*-bis(2,6-dimethylphenyl)-2,6-pyridinedicarboxamide ligand, as clearly evidenced by the presence of the carboxamide NH signal at 9.10 ppm (fig. A.40). It was thus not possible to experimentally determine the pK_a values of **44-46a(H)** and in turn could not calculate the BDFE_{O–H} for **44-46a(H)**.

DFT Methods

All calculations have been performed using the Amsterdam Density Functional (ADF)^{52,53} and QUILD⁵⁴ programs. Molecular orbitals were expanded in an uncontracted set of Slater type orbitals (STOs) of triple- ζ quality with double polarization functions (TZ2P), or the TDZP basis set which consists of triple- ζ quality on the metal and double- ζ quality on all other atoms, in both cases including one polarization function.^{55,56} Core electrons were not treated explicitly during the geometry optimizations (frozen core approximation⁵³). An auxiliary set of *s*, *p*, *d*, *f*, and *g* STOs was used to fit the molecular density and to represent the Coulomb and exchange potentials accurately for each SCF cycle. Geometries of all possible spin states were optimized with the QUILD⁵⁴ program using adapted delocalized coordinates until the maximum gradient component was less than 10^{-4} a.u.. Energies, gradients and Hessians (for vibrational frequencies) were calculated using BP86-D3,⁵⁷⁻⁵⁹ in all cases by including solvation effects through the COSMO⁶⁰ dielectric continuum model with appropriate parameters for each solvent used (in this acetone was used).⁶¹

Scalar relativistic corrections have been included self-consistently in all calculations by using the zeroth-order regular approximation (ZORA).⁶² The geometry optimizations at the BP86-D3 level were performed with the TDZP basis set. Subsequent single-point calculations (with the all-electron TZ2P basis set) have been performed with S12g, S12h,⁶³ and MVS.⁶⁴ For all calculations carried out with BP86-D3 the Becke^{65,66} grid of normal quality was used; calculations performed with S12g and S12h were performed with a Becke grid of very good quality, and for MVS a five times radial-grid boost was applied. All DFT calculations were performed using the unrestricted Kohn-Sham scheme. The choice for using BP86-D3/TDZP for the geometry optimizations was based on a recent study⁶⁷ where it was shown that both BP86-D3/TDZP and S12g/TZ2P performed best for a set of 16 Fe^{III/IV} (oxo/peroxo/hydroxo) complexes. However, because of the lower needs of integration accuracy (normal for BP86-D3 vs. very good for S12g) a considerable speed-up can be achieved by using BP86-D3/TDZP.

References

- (1) Pirovano, P.; Farquhar, E. R.; Swart, M.; McDonald, A. R. *J. Am. Chem. Soc.* **2016**, *138*, 14362–14370.
- (2) Huang, D.; Holm, R. H. *J. Am. Chem. Soc.* **2010**, *132*, 4693–4701.
- (3) Patra, A. K.; Mukherjee, R. *Inorg. Chem.* **1999**, *38*, 1388–1393.
- (4) Haines, R.; McAuley, A. *Coord. Chem. Rev.* **1981**, *39*, 77–119.
- (5) Collins, T. J.; Nichols, T. R.; Uffelman, E. S. *J. Am. Chem. Soc.* **1991**, *113*, 4708–4709.
- (6) Jacobs, S. A.; Margerum, D. W. *Inorg. Chem.* **1984**, *23*, 1195–1201.
- (7) Stuart, J. N.; Goerges, A. L.; Zaleski, J. M. *Inorg. Chem.* **2000**, *39*, 5976–5984.
- (8) Lovecchio, F. V.; Gore, E. S.; Busch, D. H. *J. Am. Chem. Soc.* **1974**, *96*, 3109–3118.
- (9) Kruger, H. J.; Peng, G.; Holm, R. H. *Inorg. Chem.* **1991**, *30*, 734–742.
- (10) Alonso, P. J.; Falvello, L. R.; Forniés, J.; Martín, A.; Menjón, B.; Rodríguez, G. *Chem. Commun.* **1997**, *2*, 503–504.
- (11) Ottenwaelder, X.; Ruiz-García, R.; Blondin, G.; Carasco, R.; Cano, J.; Lexa, D.; Journaux, Y.; Aukauloo, A. *Chem. Commun.* **2004**, 504–505.
- (12) Colpas, G. J.; Maroney, M. J.; Bagyinka, C.; Kumar, M.; Willis, W. S.; Suib, S. L.; Mascharak, P. K.; Baidya, N. *Inorg. Chem.* **1991**, *30*, 920–928.
- (13) Kundu, S.; Pfaff, F. F.; Miceli, E.; Zaharieva, I.; Herwig, C.; Yao, S.; Farquhar, E. R.; Kuhlmann, U.; Bill, E.; Hildebrandt, P.; Dau, H.; Driess, M.; Limberg, C.; Ray, K. *Angew. Chem. Int. Ed.* **2013**, *52*, 5622–5626.
- (14) Cho, J.; Kang, H. Y.; Liu, L. V.; Sarangi, R.; Solomon, E. I.; Nam, W. *Chem. Sci.* **2013**, *4*, 1502–1508.
- (15) Davidson, G.; Choudhury, S. B.; Gu, Z.; Bose, K.; Roseboom, W.; Albracht, S. P. J.; Maroney, M. J. *Biochemistry* **2000**, *39*, 7468–7479.
- (16) Haumann, M.; Porthun, A.; Buhrke, T.; Liebisch, P.; Meyer-Klaucke, W.; Friedrich, B.; Dau, H. *Biochemistry* **2003**, *42*, 11004–11015.
- (17) Cho, J.; Sarangi, R.; Annaraj, J.; Kim, S. Y.; Kubo, M.; Ogura, T.; Solomon, E. I.; Nam, W. *Nat. Chem.* **2009**, *1*, 568–572.
- (18) Yiu, D. T. Y.; Lee, M. F. W.; Lam, W. W. Y.; Lau, T.-C. *Inorg. Chem.* **2003**, *42*, 1225–1232.
- (19) Mayer, J. M. *Acc. Chem. Res.* **2011**, *44*, 36–46.
- (20) Roth, J. P.; Yoder, J. C.; Won, T.-J.; Mayer, J. M. *Science* **2001**, *294*, 2524–2526.
- (21) Mayer, J. M. *Annu. Rev. Phys. Chem.* **2004**, *55*, 363–390.
- (22) Dasgupta, P. K.; Nara, O. *Anal. Chem.* **1990**, *62*, 1117–1122.
- (23) Pines, D.; Ditzkovich, J.; Mukra, T.; Miller, Y.; Kiefer, P. M.; Daschakraborty, S.; Hynes, J. T.; Pines, E. *J. Phys. Chem. B* **2016**, *120*, 2440–2451.
- (24) Ranney, A. P.; Ziemann, P. J. *J. Phys. Chem. A* **2016**, *120*, 2561–2568.
- (25) Manner, V. W.; Dipasquale, A. G.; Mayer, J. M. *J. Am. Chem. Soc.* **2008**, *3*, 7210–7211.
- (26) Warren, J. J.; Tronic, T. A.; Mayer, J. M. *Chem. Rev.* **2010**, *110*, 6961–7001.
- (27) Blanksby, S. J.; Ellison, G. B. *Acc. Chem. Res.* **2003**, *36*, 255–263.
- (28) Dhar, D.; Yee, G. M.; Spaeth, A. D.; Boyce, D. W.; Zhang, H.; Dereli, B.; Cramer, C. J.; Tolman, W. B. *J. Am. Chem. Soc.* **2016**, *138*, 356–368.
- (29) Baglia, R. A.; Prokop-Prigge, K. A.; Neu, H. M.; Siegler, M. A.; Goldberg, D. P. *J. Am. Chem. Soc.* **2015**, *137*, 10874–10877.
- (30) Matsuo, T.; Mayer, J. M. *Inorg. Chem.* **2005**, *44*, 2150–2158.
- (31) Bryant, J. R.; Mayer, J. M. *J. Am. Chem. Soc.* **2003**, *125*, 10351–10361.
- (32) Brandi, P.; Galli, C.; Gentili, P. *J. Org. Chem.* **2005**, *70*, 9521–9528.
- (33) Mayer, J. M. *J. Phys. Chem. Lett.* **2011**, *2*, 1481–1489.
- (34) Draksharapu, A.; Angelone, D.; Quesne, M. G.; Padamati, S. K.; Gómez, L.; Hage, R.; Costas, M.; Browne, W. R.; de Visser, S. P. *Angew. Chem. Int. Ed.* **2015**, *54*, 4357–4361.
- (35) Westheimer, F. H. *Chem. Rev.* **1961**, *61*, 265–273.
- (36) Kwart, H. *Acc. Chem. Res.* **1982**, *15*, 401–408.

- (37) Mandal, D.; Ramanan, R.; Usharani, D.; Janardanan, D.; Wang, B.; Shaik, S. *J. Am. Chem. Soc.* **2015**, *137*, 722–733.
- (38) Mandal, D.; Shaik, S. *J. Am. Chem. Soc.* **2016**, *138*, 2094–2097.
- (39) Yin, G.; Danby, A. M.; Kitko, D.; Carter, J. D.; Scheper, W. M.; Busch, D. H. *J. Am. Chem. Soc.* **2008**, *130*, 16245–16253.
- (40) Klinker, E. J.; Shaik, S.; Hirao, H.; Que, L. *Angew. Chem. Int. Ed.* **2009**, *48*, 1291–1295.
- (41) Wang, D.; Zhang, M.; Bühlmann, P.; Que, L. *J. Am. Chem. Soc.* **2010**, *132*, 7638–7644.
- (42) Goldsmith, C. R.; Jonas, R. T.; Stack, T. D. P. *J. Am. Chem. Soc.* **2002**, *124*, 83–96.
- (43) Donoghue, P. J.; Tehranchi, J.; Cramer, C. J.; Sarangi, R.; Solomon, E. I.; Tolman, W. B. *J. Am. Chem. Soc.* **2011**, *133*, 17602–17605.
- (44) Dhar, D.; Tolman, W. B. *J. Am. Chem. Soc.* **2015**, *137*, 1322–1329.
- (45) Arunkumar, C.; Lee, Y.-M.; Lee, J. Y.; Fukuzumi, S.; Nam, W. *Chem. Eur. J.* **2009**, *15*, 11482–11489.
- (46) Bunting, J. W.; Luscher, M. A. *Can. J. Chem.* **1988**, *66*, 2524–2531.
- (47) Bruker APEX v2014.11-0, Bruker AXS Inc., Madison, Wisconsin, USA.
- (48) SHELXL-2014, Bruker AXS Inc., Madison, Wisconsin, USA.
- (49) Sheldrick, G. *Acta Crystallogr. Sect. A* **2008**, *64*, 112–122.
- (50) Stoll, S.; Schweiger, A. *J. Magn. Reson.* **2006**, *178*, 42–55.
- (51) Ravel, B.; Newville, M. *J. Synchrotron Radiat.* **2005**, *12*, 537–541.
- (52) Baerends, E. J. et al. ADF2013.01.; SCM, Amsterdam, 2013.
- (53) Te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Fonseca Guerra, C.; van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931–967.
- (54) Swart, M.; Bickelhaupt, F. M. *J. Comput. Chem.* **2008**, *29*, 724–734.
- (55) Van Lenthe, E.; Baerends, E. J. *J. Comput. Chem.* **2003**, *24*, 1142–1156.
- (56) Chong, D. P.; van Lenthe, E.; van Gisbergen, S.; Baerends, E. J. *J. Comput. Chem.* **2004**, *25*, 1030–1036.
- (57) Becke, A. *Phys. Rev. A* **1988**, *38*, 3098–3100.
- (58) Perdew, J. *Phys. Rev. B* **1986**, *33*, 8822–8824. Erratum: Ibid. 34, 7406.
- (59) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104.
- (60) Klamt, A.; Schüürmann, G. *J. Chem. Soc., Perkin Trans. 2* **1993**, 799–805.
- (61) Swart, M.; Räsler, E.; Bickelhaupt, F. M. *Eur. J. Inorg. Chem.* **2007**, 2007, 3646–3654.
- (62) Van Lenthe, E.; Baerends, E.; Snijders, J. *J. Chem. Phys.* **1993**, *99*, 4597–4610.
- (63) Swart, M. *Chem. Phys. Lett.* **2013**, *580*, 166–171.
- (64) Sun, J.; Perdew, J. P.; Ruzsinszky, A. *Proc. Natl. Acad. Sci. U.S.A.* **2015**, *112*, 685–689.
- (65) Franchini, M.; Philipsen, P. H. T.; Visscher, L. *J. Comput. Chem.* **2013**, *34*, 1819–1827.
- (66) Becke, A. *J. Chem. Phys.* **1988**, *88*, 2547–2553.
- (67) Gruden, M.; Vlahovic, F.; Stepanovic, S.; Swart, M. *J. Chem. Inf. Model.* **2016**, submitted.

Chapter 4

Modulation of the Coordination Environment of Nickel(II) and (III) Pyridinedicarboxamidate Complexes

The XRD data collection and structure solutions and refinements were done by Dr Brendan Twamley (Trinity College Dublin); Prof. Robert Barkley (Trinity College Dublin) provided access and training to the EPR spectrometer.

4.1 Introduction

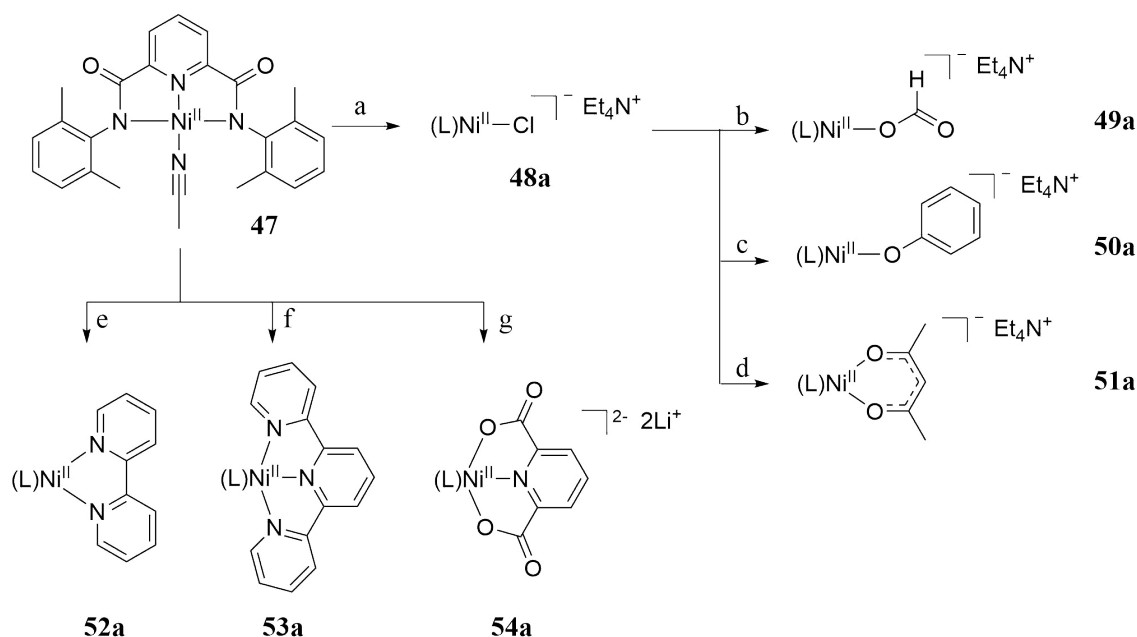
The work described in chapter 3 demonstrated that $\text{Ni}^{\text{III}}\text{--O--X}$ complexes are competent oxidants, and three such species based on the $[\text{Ni}(\text{pyN}_2^{\text{Me}_2})]$ core were compared. I set out to synthesise further $[\text{Ni}(\text{L})(\text{pyN}_2^{\text{Me}_2})]$ derivatives with a wider range of neutral or anionic L ligands, with the goal of elucidating the relationships between structure and spectral properties, and between structure and reactivity. One particular perspective was to better understand the relationship between the structures and EPR spectra, especially with regard to the relationship between molecular geometry and both g tensor symmetry and entity of hyperfine coupling.

Secondly, multiple factors affecting the oxidative reactivity of Ni^{III} species could be investigated: total charge, ligand basicity, coordination number and type of donor atom (*i.e.* O vs N vs Cl) can all be taken in consideration. A important issue was that, in the reactions of **44-45b** with phenols and hydrocarbons, the fate of the transferred H atom (section 3.4.1) could not be ascertained. Each complex had two potential O acceptors in the terminal O ligand (e.g. in $\text{CH}_3\text{C}(\text{O})\text{O-}$), as well as the highly basic carboxamidate nitrogens: examining complexes without an O ligand is particularly interesting in this regard, as it would allow to discriminate between reactivity centred on the $\text{pyN}_2^{\text{Me}_2}$ ligand. For these purposes $[\text{Ni}(\text{L})(\text{pyN}_2^{\text{Me}_2})]$ complexes with $\text{L} = ^-\text{Cl}, ^-\text{OCHO}, ^-\text{OPh}$, acetylacetonate, bipyridine, terpyridine and 2,6-pyridinedicarboxylate (sch. 4.1) were studied.

4.2 Synthesis and characterisation of nickel(II) complexes

4.2.1 Synthesis

The general method used to synthesise a series of $[\text{Ni}(\text{L})(\text{pyN}_2^{\text{Me}_2})]$ complexes was the substitution of the acetonitrile ligand in $[\text{Ni}(\text{CH}_3\text{CN})(\text{pyN}_2^{\text{Me}_2})]$, compound **47** (sch. 4.1). This improved the previously reported syntheses of $[\text{Ni}(\text{Cl})(\text{pyN}_2^{\text{Me}_2})]\text{Et}_4\text{N}$ (**48a**) and $[\text{Ni}(\text{OCHO})(\text{pyN}_2^{\text{Me}_2})]\text{Et}_4\text{N}$ (**49a**), whose preparation from $[\text{Ni}(\text{OH})(\text{pyN}_2^{\text{Me}_2})]\text{Et}_4\text{N}$, required longer time and only had modest yields.¹ **48a** was obtained by the addition of $\text{Et}_4\text{NCl} \cdot \text{H}_2\text{O}$ (1.05 eq.) to a solution of **47** in CH_3CN , followed by crystallisation of the product by the addition of Et_2O ; dark red crystals were obtained in 85% yield. From this complex, $[\text{Ni}(\text{OCHO})(\text{pyN}_2^{\text{Me}_2})]\text{Et}_4\text{N}$ (**49a**), $[\text{Ni}(\text{OPh})(\text{pyN}_2^{\text{Me}_2})]\text{Et}_4\text{N}$ (**50a**), and $[\text{Ni}(\text{acac})(\text{pyN}_2^{\text{Me}_2})]\text{Et}_4\text{N}$ (**51a**, *acac* = acetylacetonate) could be obtained. **48a** was formed *in situ*, without isolating it, and subsequently the chloride ligand was exchanged by the addition of KOCHO , NaOPh or $\text{Na}(\text{acac})$ respectively. After separation of the resulting



Scheme 4.1. Synthetic routes to the Ni^{II} complexes **48-54a**. (a) $\text{Et}_4\text{NCl} \cdot \text{H}_2\text{O}$, CH_3CN ; (b) KOCHO , CH_3OH ; (c) NaOPh , CH_3OH ; (d) $\text{Na}(\text{acac})$, DMF ; (e) bpy , CH_3CN ; (f) terpy , CH_3OH . All compounds were crystallised from CH_3CN and Et_2O , except for **50a** (DMF and Et_2O), **53a** (CH_3OH and Et_2O), and **54a** (CH_3OH and MTBE).

KCl or NaCl precipitates by filtration, crystals of each compound were obtained by layering of Et_2O over acetonitrile solutions of the crude materials, in yields of 76% (**49a**), 68% (**50a**), and 55% (**51a**).

The synthesis of **51a** was conducted under anhydrous conditions and in an inert atmosphere. In fact, early synthesis attempts under the laboratory atmosphere yielded an impure product, which after repeated crystallisations was identified, by ^1H NMR, to contain the $\text{Ni}^{\text{II}}-\text{OAc}$ complex **45a**. Furthermore, red single crystals were recovered from the crude product, which were shown by XRD experiment to be 1:1 cocrystals of **51a** and **45a** (fig. 4.1). The acetate group could originate either from the oxidation of acetylacetonate by atmospheric O_2 , or by its hydrolysis, through a retro-Claisen mechanism (sch. 4.2).

There are reports of Ni^{II} complexes which contain β -diketonate ligands that are spontaneously oxidised, on exposure to O_2 , to two carboxylates and CO .²⁻⁴ The nickel-dependent enzyme acireductone dioxygenase,⁵ as well, promotes the oxidation of its β -diketonate substrate in the same manner. These molecules however all have a CHOH group between the two carbonyl moieties of the diketonate, which is fundamental to the reaction, forming the CO molecule after cleaving of two $\text{C}-\text{C}$ bonds. A $[\text{D}_6]\text{DMSO}$ solution of **51a** did not appreciably decay over the course of two days, when exposed to air; conversely, after 12 hours for the addition of 0.1 mL of D_2O , the formation of **45a** was evident in the ^1H

NMR spectrum by the appearance of the characteristic peak of bound -OAc at 0.78 ppm (fig. A.62). For this reason, one can propose that binding to the Lewis acidic Ni centre favours the nucleophilic attack of H_2O on one of the carbonyl groups, initiating hydrolysis via the retro-Claisen mechanism to give acetate and acetone.

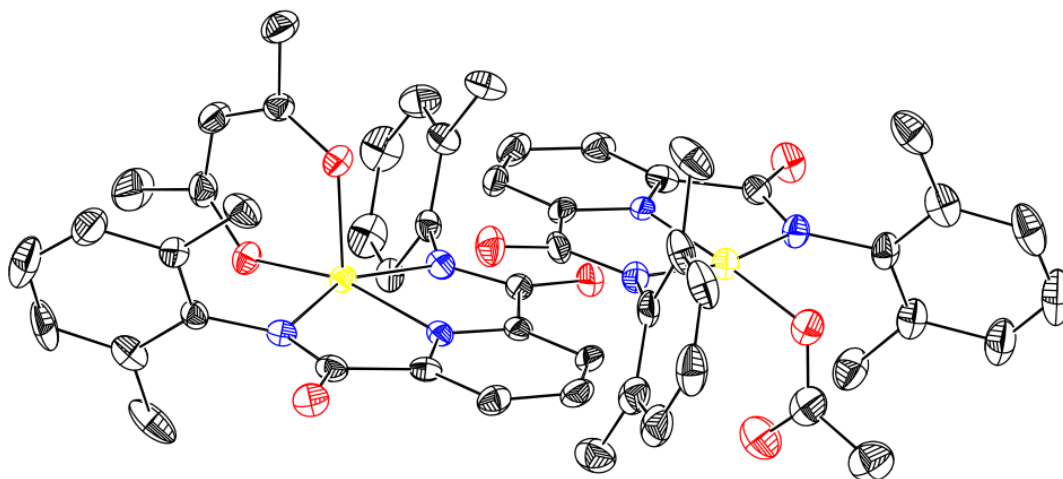
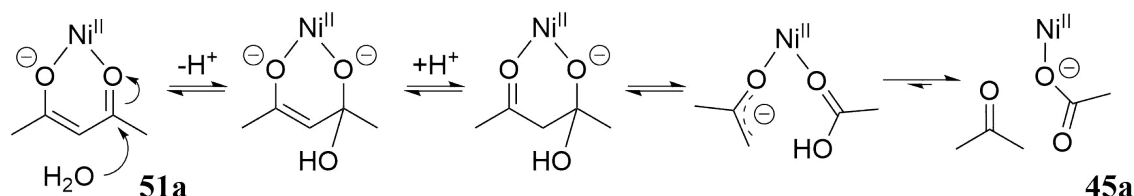


Figure 4.1. ORTEP plots (at 50% probability level) of the X-ray structure of the **51a.45a** cocrystal. Hydrogen atoms, the counterions (Et_4N^+) and H_2O of crystallisation have been omitted for clarity.



Scheme 4.2. Hypothetical retro-Claisen mechanism for the formation of acetate from **51a**.

$[\text{Ni}(\text{bpy})(\text{pyN}_2^{\text{Me}_2})]$ (**52a**, *bpy* = 2,2'-bipyridine) and $[\text{Ni}(\text{terpy})(\text{pyN}_2^{\text{Me}_2})]$ (**53a**, *terpy* = 2,2';6',2''-terpyridine), were prepared by the simple addition of the neutral ligands *bpy* and *terpy* (1 eq.) to solutions of **47** in CH_3CN (for **52a**) or CH_3OH (for **53a**); crystals of both were obtained by the slow diffusion of Et_2O in the solution, in 78% and 75% yields respectively.

Finally, the dianionic complex $[\text{Ni}(\text{2,6-dipic})(\text{pyN}_2^{\text{Me}_2})]\text{Li}_2$ (**54a**, 2,6-*dipic* = 2,6-pyridine-dicarboxylate) was generated by the reaction of **47** with $\text{Li}_2(\text{2,6-dipic})$ (1.2 eq.) in CH_3OH . After evaporation of the solvent, the light brown impure product was washed with ethyl acetate, and crystallised from CH_3OH and methyl-*tert*-butylether, to give the product in

64% yield. All the complexes were characterised via single crystal X-Ray diffraction, ESI MS, NMR, UV-Vis, FTIR spectroscopies, and cyclic voltammetry.

4.2.2 Crystal structures

The four coordinate compounds **48a**, **49a** (both structures were previously reported¹), and **50a** had square planar geometries (fig. 4.2), with the geometry index⁶ $\tau_4 = 0.11$, 0.07 and 0.14 respectively, in line with other reported $[\text{Ni}(\text{X})(\text{pyN}_2^{\text{Me}_2})]$ complexes (chapter 3 and reference¹). The terminal $-\text{OPh}$ and $-\text{OCHO}$ ligands were perpendicular to the NiN_3O coordination plane.

Compounds **51a** and **52a** displayed a square pyramidal geometry (fig. 4.2), with the three N donors from $\text{pyN}_2^{\text{Me}_2}$ and one N/O donor from the second ligand in the basal plane, and τ_5 values⁷ of 0.22 and 0.35 respectively. Of the two independent molecules of **52a** in the asymmetric unit, one was refined with a CH_3CN ligand bound in the sixth coordination position, with 10% occupancy. Nevertheless, the ^1H NMR spectra of **52a** in either CDCl_3 or CH_3CN did not show differences (fig. A.64), *i.e.* the same number of signals were present, with only minor solvent-induced shifts. An octahedral **52a**(CH_3CN) would be expected to have more significant shifts, and possibly two inequivalent pyridine groups giving rise to a higher number of signals. From this it can be concluded that the free coordination position was not extensively occupied in solution.

53a and **54a** both had distorted octahedral geometries, (fig. 4.2), with double axial bending,⁸ *i.e.* two of the L–Ni–L axes had angles smaller than 180° . This distortion was caused by the tridentate, meridional ligands $\text{pyN}_2^{\text{Me}_2}$, *terpy* and *2,6-dipic* having bite angles smaller than 90° for each *cis* pair of donor atoms. In **54a** there was an interaction between one of the carboxylate C=O groups and one of the lithium counterions, whose coordination is completed by H_2O and CH_3OH molecules.

The bond distances in the $[\text{Ni}(\text{pyN}_2^{\text{Me}_2})]$ core were essentially invariant in the square planar complexes, whereas for the higher coordinate **51–54a** there is a lengthening of 0.1–0.2 Å of both the $\text{Ni-N}_{\text{amide}}$ and the $\text{Ni-N}_{\text{pyridine}}$ coordination bonds (table 4.1). In the square pyramidal structures, the apical ligands were significantly more distant than the equatorial, even if the *acac* and *bpy* of **51a** and **52a** are symmetrical. Even in the pseudo-octahedral compounds, there was a marked elongation for the bond distances of the ligands above and below the $[\text{Ni}(\text{pyN}_2^{\text{Me}_2})]$ plane. For example in **53a**, the Ni-N (“pseudo-apical”) distance was 2.10 Å, vs. 2.01 for Ni-N (“pseudo-equatorial”), in spite of both N donors being pyridine groups.

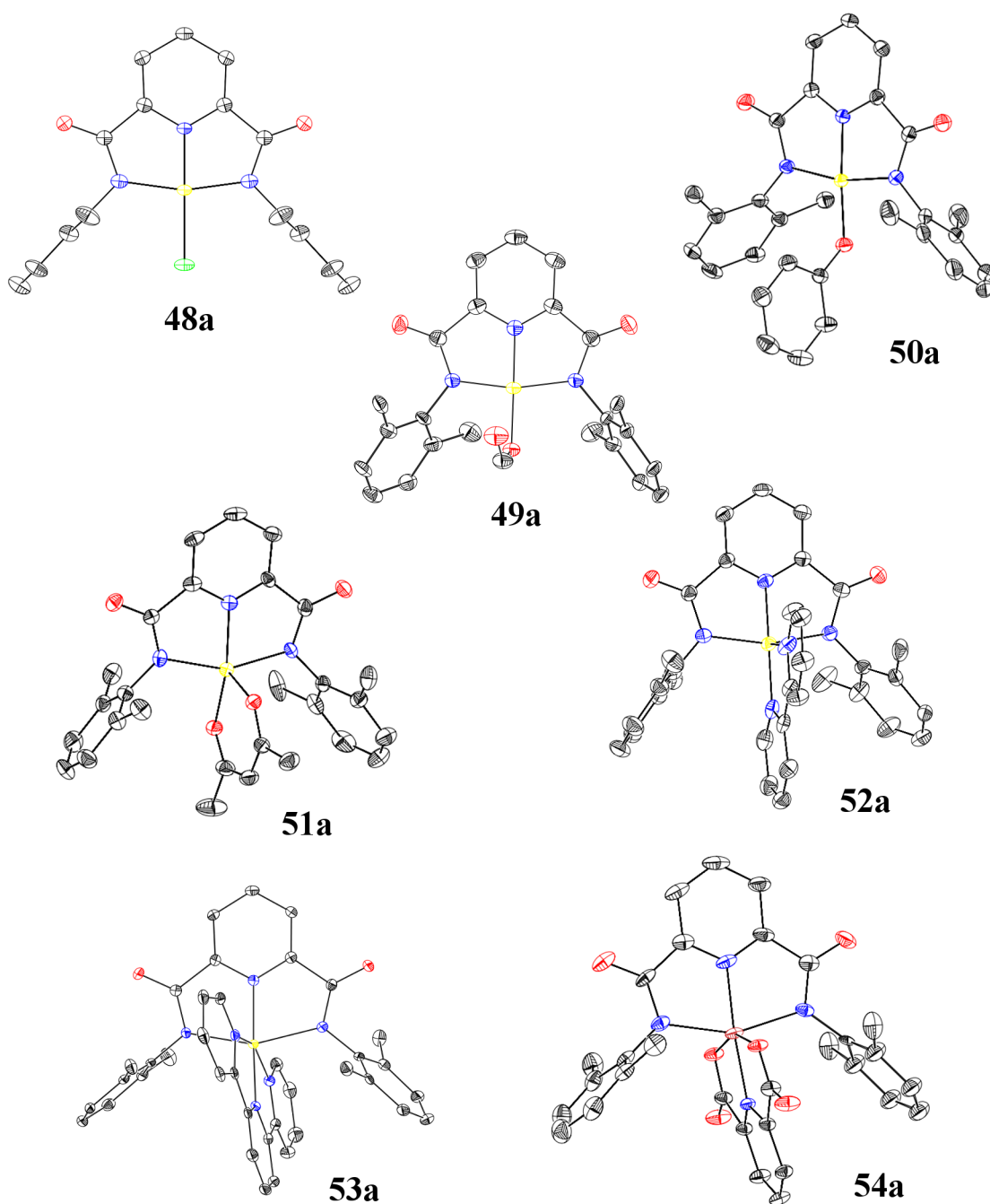


Figure 4.2. ORTEP plots (at 50% probability level) of the X-ray structures of **48-54a**. **48-49a** previously reported.¹ Hydrogen atoms, the counterions (Et_4N^+) for **48-51** and Li^+ for **54**, solvents of crystallisation have been omitted for clarity; disorder is not shown.

In summary, the XRD structures gave confirmation of the structure assignments and geometry of the new Ni^{II} compounds. Furthermore, ions corresponding to the nickel-containing portion of the compounds were identified for all in ESI MS (in negative mode for the anionic **48-51a** and **54a**, and in positive mode for the neutral **52-53a**), confirming the stability of the structures after dissolution.

Table 4.1. Average bond distances (Å) and angles (°) for **48-54a**.

	48a ¹	49a ¹	50a	51a	52a	53a	54a
Ni–N _{pyridine}	1.796(7)	1.801(7)	1.826(2)	1.953(1)	1.885(2)	1.987(2)	1.977(4)
Ni–N _{amide}	1.912(5)	1.888(5)	1.91(1)	2.038(2)	1.976(3)	2.172(5)	2.13(3)
Ni–O/N/Cl _{plane}	2.174(2)	1.856(5)	1.848(2)	1.946(1)	1.967(3)	2.005(2)	1.983(4)
Ni–O/N _{apical}				2.005(1)	2.161(3)	2.120(2), 2.090(2)	2.094(3), 2.170(3)
N _{pyridine} –Ni–O/N _{apical}				99.59(5)	80.0(1)	102(7)	102(3)
N _{amide} –Ni–O/N _{apical}				99.0(7)	97.3(4)	93(5)	92.6(14)
O/N _{plane} –Ni–O/N _{apical}				93.95(5)	99.7(1)	77.66(7)	77.6(7)
N _{pyridine} –Ni–N _{amide}	82.24(12)	82.92(14)	82.8(2)	79.0(2)	80.95(5)	77.39(13)	77.8(5)
N _{amide} –Ni–O/N/Cl _{plane}	97.76(12)	97.17(14)	97.2(5)	99.0(4)	99.1(1)	103(4)	102(6)
N _{amide} –Ni–N _{amide}	164.5(2)	165.4(3)	165.56(8)	153.56(5)	158.4(1)	153.81(6)	155.2(1)
N _{pyridine} –Ni–O/N/Cl _{plane}	180	177.0(3)	174.8(1)	166.46(5)	179.6(1)	171.80(7)	172.9(2)
N _{apical} –Ni–N _{apical}						155.20(6)	155.5(2)
τ_4/τ_5	0.11	0.07	0.14	0.22	0.35		

4.2.3 Spectroscopy and magnetic properties

The ¹H NMR spectra of **48a**, **49a** and **50a** were analogous to those of previously reported [Ni(X)(pyN₂^{Me2})] complexes, and indicative of a diamagnetic, low-spin electronic structure (figs. A.55 to A.60). All different aromatic protons in the phenoxo group of **50a** generated distinct signals, indicating that they are neither exchanged by symmetry (consistently with the solid state structure, fig. 4.2), nor by fast rotation about the Ni–O^{Ph} bond on the NMR timescale.

By contrast, all five and six coordinate complexes **51-54a** displayed peak broadening and shifts typical of paramagnetic species (fig. 4.3). With the exception of **53a**, the peaks were sufficiently sharp and well-resolved, so that integration and cross-comparison allowed for the partial assignments of the peaks. Typically among high-spin Ni^{II} complexes, tetrahedral and 5-coordinate complexes have relaxation times that are long enough for reasonably good spectra, while this is more difficult for the octahedral geometry.⁹

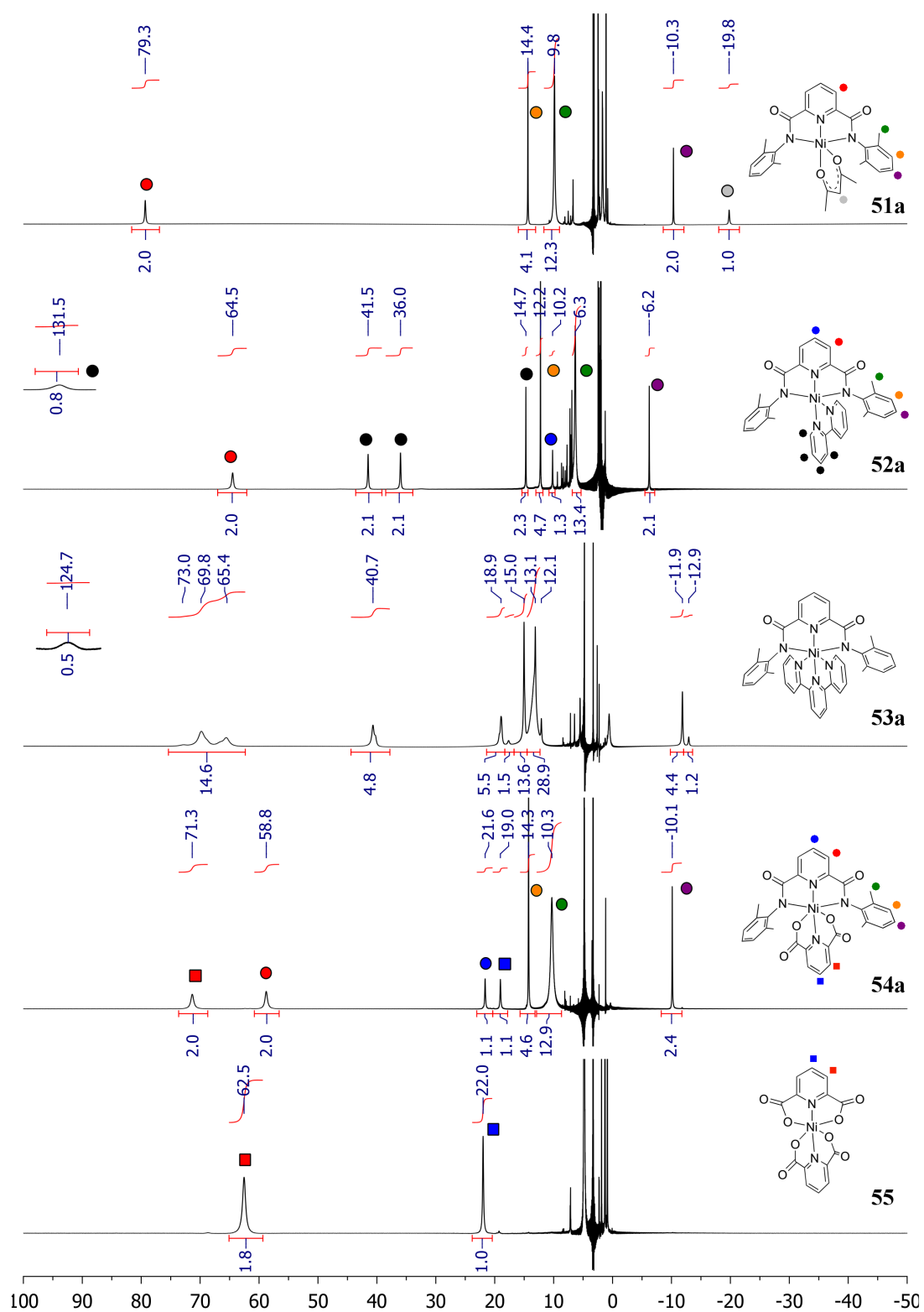
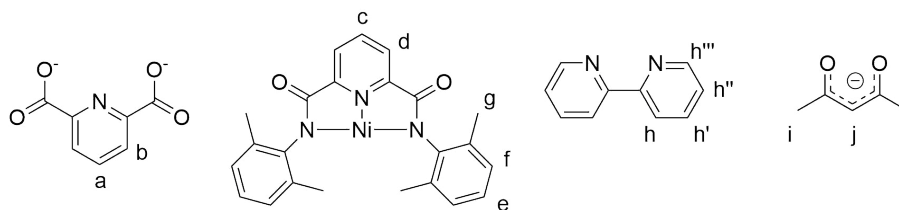


Figure 4.3. ^1H NMR spectra of **51a** ($[\text{D}_6]\text{DMSO}$), **52a** (CD_3CN), **53-54a** and **55** (CD_3OD), with partial assignment of the paramagnetically shifted peaks.



Scheme 4.3. Labels for the protons used in the assignment of the ^1H NMR spectra of **51–54a**.

Assignment of the signals was facilitated by comparison with the spectrum of $[\text{Ni}(\text{2,6-dipic})_2]\text{Li}_2$ (**55**), a few crystals of which were fortuitously obtained from an unsuccessful attempt of obtaining single crystals of **54a**. **55** had a simple two-signal spectrum, (similar to previously reported compounds containing the same anion¹⁰) with a peak at 63 ppm assigned to the *meta* protons of the pyridine ring (H^{a} , sch. 4.3), and one at 22 ppm, assigned to the *para* protons (H^{b}), on the basis of integration (fig. 4.3). These two signals were present also in **54a** (which contains the 2,6-*dipic* ligand). A similar signal at $\sim 60\text{--}80$ corresponding to the *meta*-pyridine protons of the $\text{pyN}_2^{\text{Me}_2}$ ligand (H^{d}) was present in all complexes **51a**, **52a** and **54a**. The *para*-proton signal (H^{e}) was more mobile, at 10 ppm in **52a**, 20 ppm in **54a**, and could not be identified with certainty in **51a**.

Integration helped to identify the *para*- and *meta*- aromatic and 12 methyl protons from the aniline moieties ($\text{H}^{\text{e/f/g}}$), at $\sim -6 - -10$, $\sim 10\text{--}14$, and $\sim 6\text{--}10$ ppm respectively for all complexes. Four additional signals of two protons each were present in the spectrum of **52a**, corresponding to the *bpy* ligand (H^{h}), while only one additional, one proton signal was at -20 ppm in **51a** and was of uncertain assignment (either *para*-pyridine, H^{b} or the central proton of *acac*, H^{j}). The spectrum of **53a** presented more line broadening and overlap, and could not be assigned.

The number of signals in the spectra of **51a** and **52a** suggested a high symmetry, that is, the two halves of the *acac* and *bpy* ligands were equivalent. In the solid state structure they were in different environments (*i.e.* apical and equatorial coordination), hence the solution spectra were indicative of either a change to trigonal bipyramidal coordination, or fast dynamic exchange between the two alternative square pyramidal conformations. In fact, the methyl signals from the *acac* ligand were not observed, which could be in theory explained by excessive broadening caused by interconversion of the two position on the NMR timescale. If this were the case, a sufficiently high experiment temperature would result in a fast exchange regime, and a single sharp signal for the two groups. Variable temperature experiments between -20 and $80\text{ }^\circ\text{C}$ did not evidence the emergence of new peaks, and unfortunately instrumental factors limited the possibility of exploring a larger

temperature range; hence, the coordination geometry in solution of **51a** and **52a** could not be conclusively determined.

The magnetic moments of **51-54a** in solution were measured *via* the Evans method (table 4.2). The μ_{eff} values (**51a**: 2.99, **52a**: 2.50 **53a**: 3.07 **54a**: 3.04 μ_B) were within the typical values for penta- and hexacoordinate Ni^{II} ,¹¹ with the exception of **52a**, which was slightly lower but nevertheless indicative of a high spin d^8 ion, possessing two unpaired electrons ($S = 1$).

The different magnetic properties of the square planar nickel(II) complexes and their 4- and 5- coordinate counterparts are a consequence of their different ligand fields. A second effect was evident in their colours or, more generally, electronic absorption spectra (table 4.2 and figs. 4.5 and A.82). The square planar **48a**, **49a** and **50a**, as well as $[Ni^{II}(OH)(pyN_2^{Me_2})]$, **47** and **44-46a** (chapter 3), all had orange or red colours arising from moderately intense ($\varepsilon \approx 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) bands at 450-550 nm, as is common for nickel(II) compounds of this geometry.^{12,13} **51-54a**, conversely, had some weak, $d-d$ bands ($\varepsilon \leq 100$) at lower energy, in the 800-1000 nm region, which is again typical for 5- and 6-coordinate Ni^{II} .¹²

4.2.4 Electrochemical properties

Cyclic voltammetry was performed on the new nickel(II) complexes, as well as the $Ni-NCCCH_3$ complex **47** (chapter 3) in order to ascertain their potential for generating nickel(III) species and the effect of the different coordination numbers and basicity of ligands on the redox potentials. The experiments were done in acetone (with 20% CH_3CN for **52a** and 20% CH_3OH for **53-54a**, in order to improve solubility), with 0.1 M Bu_4NPF_6 and scan rates of 0.05 V s^{-1} .

Almost all compounds displayed in the steady state one (quasi)reversible redox wave at relatively low potentials (table 4.2 and fig. 4.4), with peak separations of 0.08-0.010 V, which can be attributed to the $Ni^{II/III}$ conversion. The exceptions were **47**, with no redox events at $E < 1$ V, and **50a**, which only had an irreversible oxidation wave at 0.26 V vs. Fc^+/Fc ; most likely its redox behaviour was complicated by the redox-active nature of the phenoxide ligand. The variation in $E_{Ni^{II/III}}^0$ can be explained on the basis of the charge of the complex, and the electron-donation from the ligands, estimated from their basicity (pK_a of their conjugate acids). The lowest values belonged to **51a** ($E_{Ni^{II/III}}^0 = -0.14$ V), which is anionic and has the most basic ligand (aqueous scale pK_a of *Hacac* = 9), and **54a** ($E_{Ni^{II/III}}^0 = -0.07$ V), which has three donors, two of which are anionic; the highest corresponded to **48a** (0.43 V) and **49a** (0.48 V). It is interesting to compare the three

Table 4.2. Spectral, magnetic, electrochemical and reactivity properties of **48-54a/b**.

	λ_{max} (nm) (ε / $M^{-1} cm^{-1}$)	$\mu_{eff.}$ (μ_B)	$E_{1/2}$ vs Fc^+/Fc (V)	g_x, g_y, g_z ($g_{av.}$)	A_{zz} (MHz)	$t_{1/2}$	k_2 2,6-DTBP at -40 °C ($M^{-1} s^{-1}$)
48a	455 (2300), 500 (1800)		0.43				
49a	455 (1200)		0.48				
50a	390 (4400), 460sh (850), 530sh (380)		0.26				
51a	380sh (1800), 770 (110), 980 (130)	2.99	-0.14				
52a	380sh (2400), 470sh (450), 850 (40)	2.50	0.26				
53a	440sh (70), 860 (100)	3.07	0.33				
54a	400sh (40), 900 (20)	3.04	-0.07				
48b	600 (7000)			2.32, 2.23, 2.00 (2.18)	110	7 h at -80 °C	
49b	530 (7500), 830 (4400)			2.25, 2.02 (2.17)		∞ at -80 °C	
51b	530 (4500), 720sh (2500)			2.32, 2.23, 2.01 (2.19)		∞ at -40 °C; 3 h at 25 °C	no reaction
52b	580 (5200), 790sh (2900)			2.19, 2.16, 2.02 (2.12)	65	1700 s at -40 °C	0.087
53b	420 (3900), 500 (4100), 680 (6600)			2.17, 2.14, 2.02 (2.11)	55	∞ at -40 °C; 30 s at 25 °C	1.29
54b	560 (6000), 700sh (5200)			2.22, 2.19, 2.01 (2.14)		∞ at -40 °C; 260 s at 25 °C	no reaction

neutral compounds **47** and **52-53a**. Clearly, the lack of a negative charge makes oxidation more arduous, as demonstrated by **47**, which was only oxidised (irreversible wave) at 1.03 V. The *bpy* and *terpy* complexes **52-53a**, however, had relatively low $E_{Ni^{II}/III}^0$ of 0.26 and 0.33 V respectively, having multiple pyridine donors which are more electron-rich than CH_3CN ; nevertheless, the 6-coordinate, dianionic **54a** had a potential that's lower by 0.4 V than **53a**.

All the complexes **48-54a** displayed further oxidation waves beginning at $E = 0.8$ V (figs. A.83 to A.89), however these are all irreversible; they may involve ligand oxidation processes, but the assignment can not be easily made. In any case, such strong oxidising conditions were not reached in the chemical oxidation methods described in the

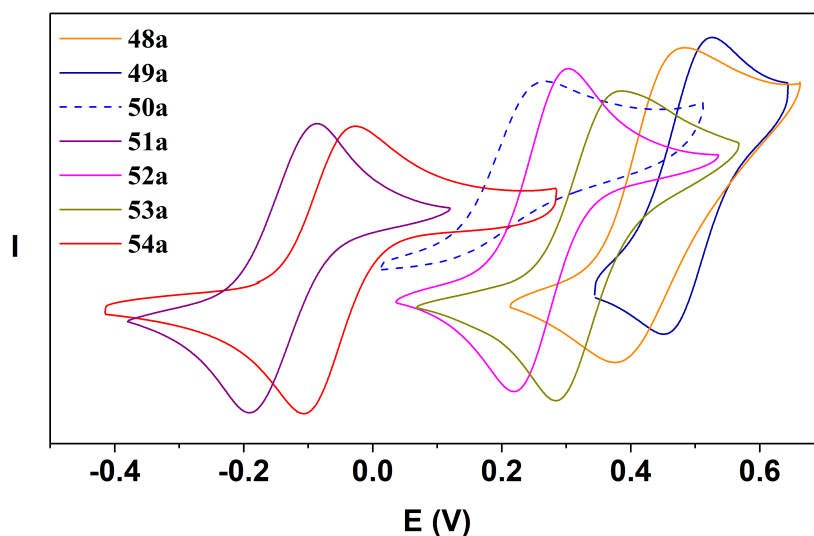


Figure 4.4. Steady state cyclic voltammograms of **48-54a** vs. Fc^+/Fc ; conditions: 0.1 mM 0.1 Bu_4NPF_6 , scan rate 0.05 V s^{-1} , room temperature.

next section. In conclusion, **48-54a** constitute a range of compounds, based on the same $[\text{Ni}^{\text{II}}(\text{pyN}_2^{\text{Me}_2})]$ core, with varied structural and electrochemical properties, suitable as starting materials for the study of Ni^{III} species; the presence of reversible redox behaviour was encouraging in suggesting that a simple one-electron oxidation without successive reaction is plausible.

4.3 Formation and characterisation of nickel(III) complexes

The generation of nickel(III) species, by the chemical oxidation of the **48-54a** precursors, was then attempted. Most of them reacted with one-electron oxidants, either tris(4-bromophenyl)ammoniumyl hexachloroantimonate (magic blue) or cerium ammonium nitrate, $((\text{NH}_4)_2[\text{Ce}^{\text{IV}}(\text{NO}_3)_6])$, CAN). The reactions were performed in thermostated cuvettes and monitored by UV-Vis spectroscopy. For the acetonitrile complex **47** and the phenoxide **50a**, suitable conditions to generate a stable oxidised species could not be found. **48a**, **49a**, and **51a**, in 0.4 mM acetone solutions, each reacted with one equivalent of magic blue at -80°C , giving new species with intense visible absorption bands (**48b**: 600 nm, **49b**: 530 and 830 nm, **51b**: 530 and 720 nm, fig. 4.6).

For the remaining three compounds, **52-54a**, optimal oxidation conditions corresponded to the addition of 2 equivalents of CAN (as an acetonitrile solution). The products had bands

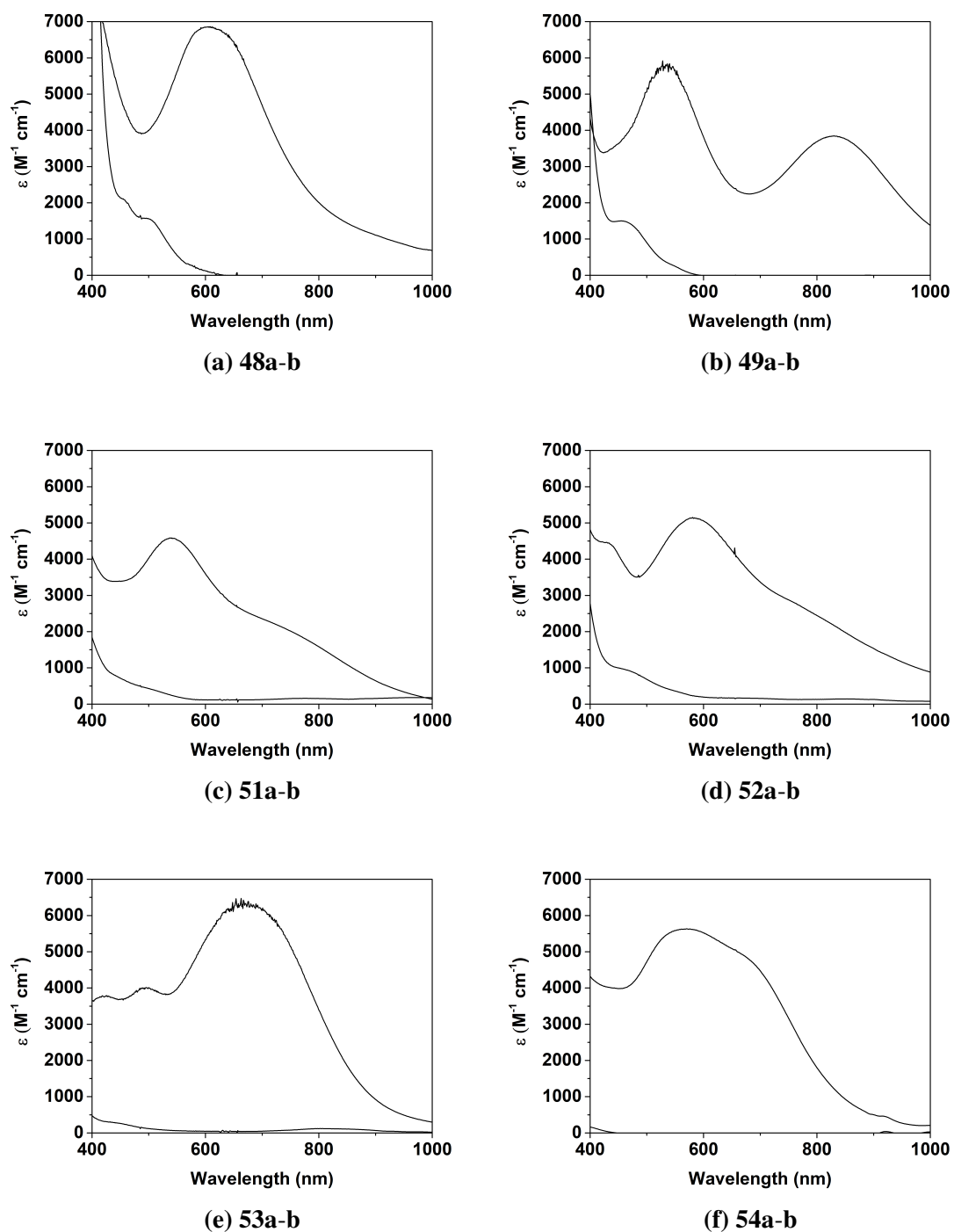


Figure 4.5. UV-Vis spectra of **48-54a-b**. Conditions: see experimental section.

at λ_{max} = 580 and 790 nm (**52b**), 680 nm (**53b**), and 560 and 700 nm (**54b**). High yields for **52b** could be obtained only at -80 °C, resulting in long reaction times (50 minutes), while **53-54b** were viable at higher temperature (-40 °C).

Because of solubility limits, the latter three compounds could not be prepared in pure acetone solutions; **52a** was dissolved in a 9/1 acetone/acetonitrile mixture, **53a** in pure CH₃OH and **54a** in 1/1 acetone/CH₃OH.

As previously observed, in the oxidations with CAN, the NO₃⁻ anion can compete with the complex's ligand for binding to the metal centre (chapter 3). Indeed, reacting more than 2 equivalents of CAN caused the formation of Ni^{III}-ONO₂ (**46b**), as evident from its absorption bands at λ_{max} = 560 and 890 nm. This problem was not encountered with **53-54a**, as the binding constants of the tridentate *terpy* and 2,6-*dipic* are likely larger.

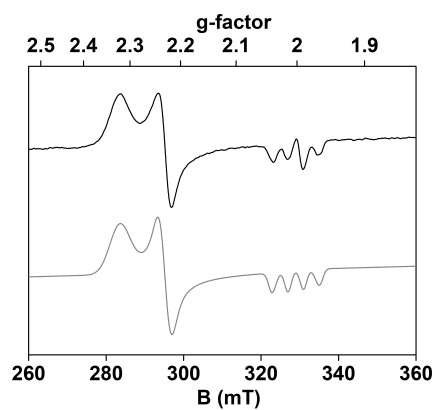
4.3.1 EPR spectroscopy

The solutions of **48-54b** generated through the aforementioned methods were analysed by EPR spectroscopy (fig. 4.6). All showed the presence of $S = 1/2$ species, with average g -values of 2.11-2.22, which are consistent with electron spin localised mainly on a low-spin, d^7 , Ni^{III} ion.¹⁴ The spectrum of the -Cl complex **48b** was rhombic, with $g = 2.32, 2.23, 2.00$, and hyperfine coupling to the ^{35/37}Cl nucleus ($I = 3/2$), evident from the four-line splitting of the z component of the signal ($A_{zz} = 110$ MHz). The formate, **49b**, was axial ($g_{\perp} = 2.25, g_{\parallel} = 2.02$), and very similar to the compounds **44-46b** described in chapters 2 and 3, although its shape could point to either a slight rhombic distortion or a small impurity.

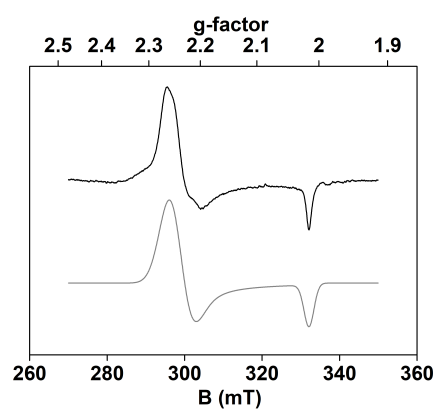
The spectrum of the *acac* complex, **51b**, on the other hand, was a mixture of a major, markedly rhombic ($g = 2.32, 2.23, 2.01$) species, plus a relatively small contamination of a second species ($\sim 15\%$ of total Ni^{III}, evaluated on the basis of the height of the signals at $g \simeq 2$). The remaining three compounds, **52-54b**, were slightly rhombic, with $g_x \simeq g_y \gg g_z$. Interestingly, **52b** showed a three-line signal shape corresponding to hyperfine coupling to one $I = 1$, ¹⁴N nucleus in the z direction ($A_{zz} = 65$ MHz); **53b** had coupling to two ¹⁴N nuclei (five-line splitting, $A_{zz} = 55$ MHz), whereas **54b** had no visible hyperfine coupling.

One of our goals was to infer the relationships between the shapes of the EPR signal shapes and the structure of the nickel(III) compounds. It is useful to this purpose, to analyse the symmetry of the nickel(II) starting materials, although there is no guarantee that their structure is maintained after oxidation.

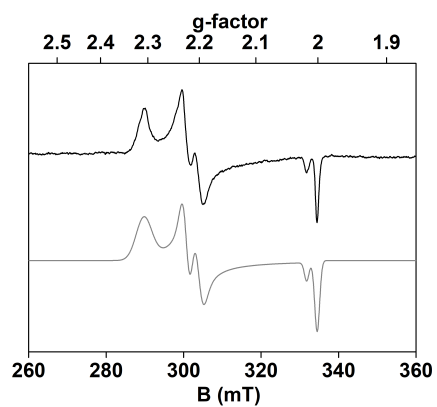
In principle, a compound will give rise to an axial signal if it has a fourfold symmetry axis, at least locally around the central metal and the neighbouring atoms on which the



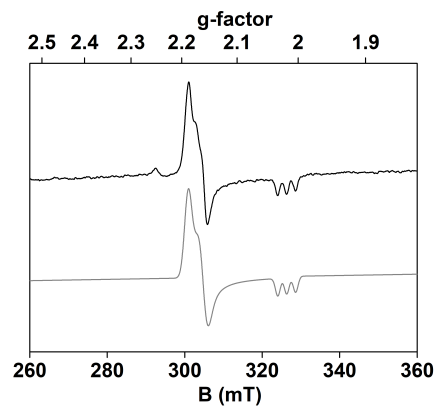
(a) 48b



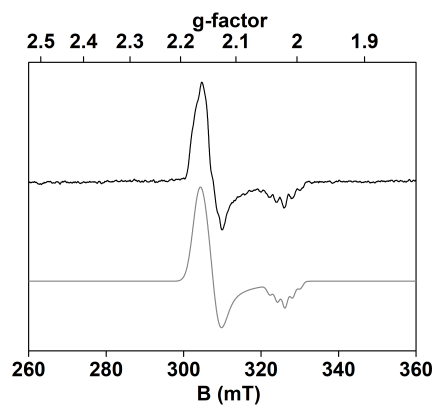
(b) 49b



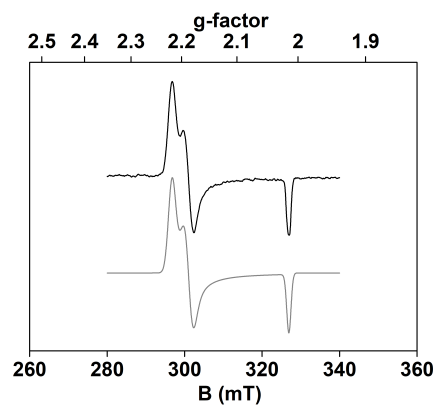
(c) 51b



(d) 52b



(e) 53b



(f) 54b

Figure 4.6. Measured (top, black) and simulated (bottom, gray) EPR spectra of 48-54b.

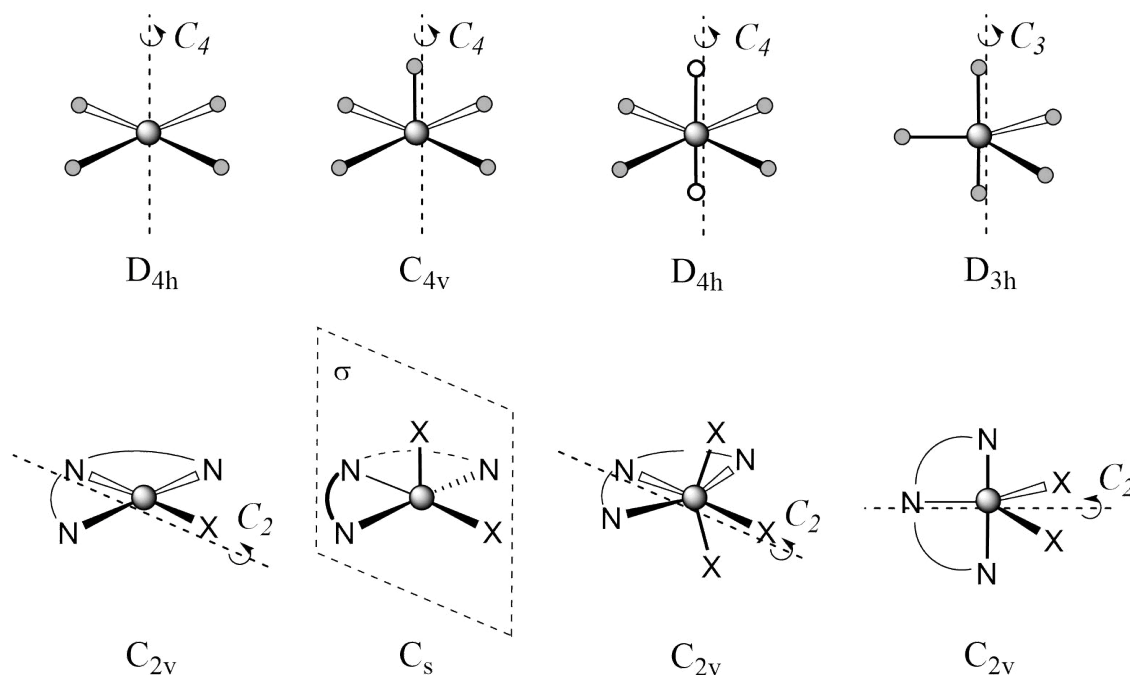


Figure 4.7. Highest order symmetry elements and point groups for the idealised coordination geometries (top) and models of complexes **51-54b** (bottom).

unpaired electron is delocalised (fig. 4.7). Hence, in the square planar case, by virtue of having a *pseudo*-D_{4h} symmetry, one would expect an axial signal, as indeed observed for **44-46b** and **49b**. In reality, the N_{amide}-Ni-N_{amide} and the N_{pyridine}-Ni-X directions are not equivalent, lowering the symmetry of the immediate coordination sphere of the metal ion to *pseudo*-D_{2h}. This is especially true for X = Cl in **48b**, as chlorine is considerably larger and has different donor properties than N/O. Similar arguments are valid for the square pyramidal structures, that is, there would be a plane with four similar N/O ligands, plus one apical ligand, to give a *pseudo*-C_{4v} symmetry. On the other hand, a trigonal bipyramidal would be at best *pseudo*-D_{3h}, and one would expect a higher rhombicity in the signal. Finally, the *pseudo*-octahedral complexes would have an analogous situation to the square planar ones, with approximate fourfold rotational symmetry in at least one direction, even if they are compressed/elongated along it (*pseudo*-D_{4h}). Of course, the actual symmetries are lowered by at least three factors: (1) distortions from the ideal coordination geometry, (2) the different nature of the donor atoms and (3) the remaining peripheral parts of the ligands, which do not interact directly with the metal.

On the basis of these arguments, the EPR spectra were consistent with complexes **49b** and **52-54b** having similar structures to those of **49a** and **52-54a** in the solid state. In particular, for **52b** a square pyramidal geometry is more likely than trigonal bipyramidal, by virtue of the fact that $g_x \simeq g_y$, suggesting a near-axial symmetry of the compound.

In contrast, **51b**'s greater separation between g_x and g_y signal was suggestive of either a trigonal bipyramidal geometry, or a bigger distortion in the coordination plane. The other unusual signal was that of **48b**, whose rhombicity can be attributed to either the different nature of the large Cl atom, lowering the symmetry in the plane, or distortion away from square planar geometry.

Resolved hyperfine coupling was observed in the three complexes **48b** and **52-53b**, in all cases only in the z component. Coupling in the other directions cannot anyway be excluded, as the $g_{x/y}$ parts of the signal display considerably larger line broadening that could mask a fine structure with small constants: for example, in the signal of **52b** the $g_{x/y}$ components had full width at half maximum (FWHM) = 70 MHz, while for the g_z FWHM was only 35 MHz. The *bpy* and *terpy* compounds **52-53b** coupled to one and two (equivalent) ^{14}N nuclei respectively, while in the *2,6-dipic* complex **54b**, which still contains a pyridine donor, no coupling was visible; the three complexes have respectively 5, 6 and 4 N donor ligands.

It can be inferred that, as a result of the particular electronic structure of the complexes, only donor atoms above and below the molecular plane formed by the $[\text{Ni}(\text{pyN}_2^{\text{Me}_2})]$ core have large hyperfine coupling. On the basis of this hypothesis, one can further deduce that the two N donors of *bpy* in **52b** are inequivalent, and support the conclusion that a (C_{2v} , with the two pyridine groups exchanged by reflection) symmetrical trigonal bipyramidal structure is not achieved in solution. This argument also suggests that the observation of large hyperfine constant A_{zz} in **48b** is not consistent with a square planar geometry. However it is plausible that the presence of the large, third row, Cl atom can significantly alter the electronic structure of the compound, and a full clarification of this issue will require a theoretical model of it.

The EPR spectra thus contributed to the understanding of the structures of nickel(III) complexes, which are otherwise too unstable for XRD determination; however, their interpretation is not conclusive on its own, and definitive elucidation of the structures will have to avail of synergies with other techniques such as EXAFS and DFT.

4.3.2 Preliminary reactivity studies

In the study of the oxidation of phenols by the four-coordinate Ni^{III} complexes **44-46b** it was found that the electron-poor $-\text{ONO}_2$ complex **46b** reacted with the highest rates (chapter 3). Unfortunately, a consistent comparison with the extended series presented here is hampered by the different conditions necessary to form and stabilise the nickel(III)

complexes. Nevertheless, both their self-decay and their reaction with an external substrate demonstrated reactivity trends.

The thermal stability of the oxidised compounds was quite varied (table 4.2), and showed that the more electron-rich compounds are more stable in the nickel(III) oxidation state, while the more electron-poor ones are more easily reduced. So, **47** only has a weak, neutral donor (CH_3CN) and could not even be oxidised; **52b**, cationic but with two donors, could be formed at $-80\text{ }^\circ\text{C}$, and had a $t_{1/2}$ of 1700 s after warming to $-40\text{ }^\circ\text{C}$; **53b** and the anionic **54b** were indefinitely stable at that temperature, and were even moderately stable ($t_{1/2} = 30\text{ s}$ and 260 s respectively) after warming to room temperature. Similarly, **51a**, with the particularly basic, bidentate *acac* ligand was the most stable ($t_{1/2} = 3\text{ h}$ at $25\text{ }^\circ\text{C}$). The electron poor complexes **48a**, **49a**, conversely, could only be formed cleanly and stabilised at low temperatures ($-80\text{ }^\circ\text{C}$).

The reactivity of **51-54b** towards 2,6-DTBP was then explored. At $-40\text{ }^\circ\text{C}$, neither the neutral, 5-coordinate **51b** nor the anionic **54b** reacted with excess 2,6-DTBP (100 eq.), while both cationic **52b** and **53b** reacted, as evidenced by the disappearance of their characteristic visible absorption bands (figs. A.92 and A.93). The reactions were *pseudo*-first order in the presence of excess 2,6-DTPB, and their rate constants (k_{obs}) were measured by exponential fitting of the decay plot. Second order rate constants (k_2) were determined by plotting k_{obs} (determined at varying substrate concentrations) against substrate concentration and calculating the slope of the resulting linear plots (figs. A.90 and A.91). **52b** (which could only be generated in low yields at $-40\text{ }^\circ\text{C}$, in 9/1 acetone/acetonitrile) reacted with $k_2 = 0.087\text{ M}^{-1}\text{ s}^{-1}$. This value is comparable with that of the $-\text{OAc}$ complex **45b** ($k_2 = 0.125\text{ M}^{-1}\text{ s}^{-1}$, measured in acetone, chapter 3). It should be noted that the two compounds have reasonably close $E_{\text{Ni}^{\text{II}}/\text{Ni}^{\text{III}}}^0$ (**52b**: 0.26 V, **45b**: 0.35 V vs. Fc^+/Fc). **53b** ($E_{\text{Ni}^{\text{II}}/\text{Ni}^{\text{III}}}^0 = 0.33\text{ V}$) reacted one order of magnitude faster, with $k_2 = 1.29\text{ M}^{-1}\text{ s}^{-1}$, in CH_3OH .

Finally, **54b**, while not reactive at $-40\text{ }^\circ\text{C}$, in 1/1 acetone/ CH_3OH , oxidised 2,6-DTBP after warming to $25\text{ }^\circ\text{C}$. Conversely, addition of xanthene (having a weak C–H bond, $\text{BDE}_{\text{C-H}} = 75.5\text{ kcal/mol}^{15}$) did not bring about the decay of **54b**; this is in contrast, with **45b**, which was a proficient hydrogen atom abstractor from hydrocarbons at $25\text{ }^\circ\text{C}$.

These observations in summary suggest that electron-rich compounds with anionic ligands (*acac* and 2,6-*dipic*) make for more stable, but worse oxidants, in line with what observed for **44-46b**. **53b** constituted a significant exception, being more reactive than **52b** in spite of a similar reduction potential and having one more donor. If the reaction proceeded through HAT, a reduction in reactivity should also be expected for the hexacoordinate complexes, by virtue of the fact that the lack of a free coordination position would hinder

the close approach of the substrate to the metal. It cannot however be assumed that the same mechanism is at play in all cases, particularly by virtue of the fact that **53b** could only be analysed in CH₃OH; the use of a protic solvent can potentially have large effects on mechanisms that involve proton migration, either in a concerted or stepwise fashion.

4.4 Conclusions

An extended series of Ni^{II} complexes based on the [Ni^{II}(pyN₂^{Me₂})] core, with different coordination numbers (4-6) and geometries, and ligands with a variety of donor groups, was synthesised and extensively characterised. The binding mode of the supporting ligand pyN₂^{Me₂} was essentially unvaried, as a meridional N₃ ligand, with the exception of minor bond lengthening caused by increased coordination numbers. The other ligand determined the coordination geometry, with the monodentate ⁻Cl, ⁻OCHO and ⁻OPh forming square planar complexes **48-50a**, the bidentate *acac* and *bpy* forming square pyramidal complexes **51-52a** and the tridentate *terpy* and *2,6-dipic* forming (*pseudo*)octahedral complexes **53-54a**. While the square planar complexes were low spin (*S*=0), 5- and 6-coordination caused a switch to high (*S* = 1) spin, evident in both spectral and magnetic properties. Interestingly, the ¹H NMR spectra of the paramagnetic compounds could in large part be analysed and assigned, thanks to their reasonably small line-broadening.

Most of the complexes could be oxidised at low temperature to generate putative Ni^{III} species **48-53b**. Analogies in the UV-Vis spectra with the previously reported compounds (chapter 3), and EPR *g*_{av.} values typical of metal-centred spin density confirmed the formation of Ni^{III}. The EPR spectra showed a complex diversity of shapes, which can be correlated to the variations in structures. Importantly, hyperfine coupling to Cl (in **48b**) and N (in **52-53b**) atoms was evident in the *g*_z components of the signals. Further characterisation is currently in progress, and will avail of DFT calculations and X-ray absorption spectroscopy.

Initial assessment of the oxidising power of complexes **48-53b**, was carried out by examining their thermal self-decay and their reactivity towards 2,6-DTBP. A wide range of behaviours was evident, with higher coordination numbers and basicity of the ligands contributing to higher stability and lower reactivity levels, most evidently for the *acac* (**51b**) and *2,6-dipic* **54b** complexes. The phenol oxidation reactions are however complicated by possible variations in mechanism, in particular with regard to **53b**, whose reaction with 2,6-DTBP was anomalously fast in CH₃OH.

Future work will be focused on gaining further insight on this reactivity. Expanding the scope of analysed substrates (i.e. using phenols with different electron-donating or

-withdrawing substituents, oxidation potentials, and steric properties) will allow to study the mechanism of oxidation in more depth, and distinguish for example between concerted PCET, or sequential ET-PT or PT-ET.

4.5 Experimental section

Physical Methods

Electronic absorption spectra were recorded on a Hewlett Packard (Agilent) 8453 diode array spectrophotometer (190–1100 nm range) in quartz cuvettes cooled using a liquid nitrogen cooled cryostat from Unisoku Scientific Instruments (Osaka, Japan). ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR analyses were performed on an Agilent MR400 instrument (400.13 MHz for ^1H NMR and 100.61 MHz for $^{13}\text{C}\{^1\text{H}\}$ NMR). ^1H NMR spectra for paramagnetic species were acquired with 64 ms acquisition time and 30 ms relaxation time. Electrospray ionization (ESI) mass spectra were acquired using a Micromass time of flight spectrometer (tof), interfaced to a Waters 2690 HPLC, or by direct injection in the mass spectrometry instrument. ATR-FTIR spectra were recorded on a Perkin-Elmer Spectrum 100 Fourier transform infrared spectrometer. Electron paramagnetic resonance spectra were recorded on a Bruker EMX spectrometer, equipped with an Oxford Instruments CE 5396, ESR9 continuous flow cryostat and an Oxford Instruments CE 5396 precision temperature controller, using liquid nitrogen cooling. Cyclic voltammetry experiments were conducted with a CH Instruments 600E electrochemical analyser, using a glassy carbon working electrode, a platinum wire counter electrode and an Ag/AgNO₃ 0.01 M reference electrode.

Materials and synthesis

Reactions with air-sensitive materials were conducted under an inert atmosphere using standard Schlenk techniques. All solvents and reagents were purchased from commercial sources and used as received, unless otherwise stated. Anhydrous solvents were obtained by sparging with argon, followed by distillation over a drying agent. CaH₂ was used for CH₃CN and CH₂Cl₂; sodium an benzophenone were used for THF and diethylether; B₂O₃ was used for acetone. Anhydrous DMF was purchased from Aldrich.

Compounds **48a** and **49a** were previously reported;¹ hereby propose alternative syntheses, starting from **47** (chapter 3), are proposed.

Spin State Measurements

The effective magnetic moments ($\mu_{eff.}$) of the Ni^{III} complexes were measured using the modified Evans method at room temperature.¹⁶ A capillary tube containing the chosen deuterated solvent (spiked with ~1% protic solvent) was inserted in the NMR tube containing

the solution of the desired compound in the same deuterated solvent. The ^1H NMR spectrum was recorded under standard conditions, and the difference between the paramagnetically shifted and the non-shifted solvent signals was measured. χ_{mol} was calculated using the equation:

$$\chi_{mol} = \frac{3\Delta\nu M}{4\pi c f}$$

in which f is the oscillator frequency (4×10^8 Hz) of the NMR spectrometer, M is the molar mass of the compound (g/mol), c is the concentration (g/mL), and $\Delta\nu$ is the difference in frequency (Hz) between the two signals. Corrections for the diamagnetic contributions of the organic ligands were subtracted using Pascal's constants,¹⁷ and $\mu_{eff.}$ was obtained as:

$$\mu_{eff.} = \sqrt{\frac{3k_B}{N_A\mu_B^2}\chi_{mol}T}$$

in which k_B is the Boltzmann constant, N_A is the Avogadro constant, μ_B is the Bohr magneton and T is the absolute temperature (K).

Synthesis of $[\text{Ni}^{\text{II}}(\text{Cl})(\text{pyN}_2^{\text{Me}_2})]\text{Et}_4\text{N}$, tetraethylammonium chloro(*N,N'*-bis(2,6-dimethylphenyl)-2,6-pyridinedicarboxamido)nickelate(II), 48a

47 (0.300 g, 0.64 mmol) was dissolved in CH_3CN (5 mL). $\text{Et}_4\text{NCl}\cdot\text{H}_2\text{O}$ (0.123 g, 0.67 mmol, 1.05 eq.) was subsequently added and the solution stirred for 10 minutes. Stirring was ceased and Et_2O (20 mL) was layered on top of the solution. Over the course of 4 days, dark red crystals of the product formed, and were recovered by decanting of the solution (0.324 g, 0.55 mmol, 85%).

δH (400 MHz, CDCl_3): 7.92 (1H, t, $J = 7.7$ Hz, 4-py), 7.59 (2H, d, $J = 7.7$ Hz, 3,5-py), 6.82–6.71 (6H, m, ArH), 2.88 (8H, q, $J = 7.3$ Hz, NCH_2CH_3), 2.42 (12H, s, ArCH_3), 0.99 (12H, m, NCH_2CH_3).

ESI-MS (m/Z): Found: -464.0680 ($[\text{Ni}(\text{Cl})(\text{pyN}_2^{\text{Me}_2})]^-$, $\text{C}_{23}\text{H}_{21}\text{ClN}_3\text{NiO}_2$ requires 464.0676).

ν_{max} (ATR-FTIR) $/\text{cm}^{-1}$: 2989 (CH), 2949 (CH), 2915 (CH), 2851 (CH), 1611, 1604s, 1583s, 1468, 1378, 1174, 1000, 833, 760, 680.

λ_{max} /nm: (acetone) 455 (ε $/\text{M}^{-1}\text{cm}^{-1}$ 2300) 500 (1800).

Synthesis of $[\text{Ni}^{\text{II}}(\text{OCHO})(\text{pyN}_2^{\text{Me}_2})]\text{Et}_4\text{N}$, tetraethylammonium formato(*N,N'*-bis(2,6-dimethylphenyl)-2,6-pyridinedicarboxamido)nickelate(II), 49a

47 (0.200 g, 0.42 mmol) was dissolved in CH_3OH (3 mL). $\text{Et}_4\text{NCl}\cdot\text{H}_2\text{O}$ (0.078 g, 0.42 mmol, 1 eq.) and KOCHO (43 mg, 0.51 mmol, 1.2 eq.) were subsequently added and the

solution stirred for 10 minutes. The methanol was removed *in vacuo* and the residue taken up in CH₃CN (3 mL). The bright red solution was filtered, and Et₂O (20 mL) was layered on top of it. Over the course of 5 days, bright red crystals of the product formed, and were recovered by decanting of the solution (0.194 g, 0.32 mmol, 76%).

δ H (400 MHz, CDCl₃): 7.90 (1H, t, J = 7.7 Hz, 4-py), 7.56 (2H, d, J = 7.7 Hz, 3,5-py), 7.06 (1H, s, OCHO), 6.86–6.64 (6H, m, ArH), 2.80 (8H, q, 7.0 Hz, NCH₂CH₃), 2.54 (12H, s, ArCH₃), 1.09 (12H, t, J = 7.0 Hz, NCH₂CH₃).

ESI-MS (m/z): Found: -474.0982 ([Ni(OCHO)(pyN₂^{Me₂})]⁻, C₂₄H₂₂N₃NiO₄ requires 474.0964).

ν_{max} (ATR-FTIR) /cm⁻¹: 3066 (CH), 3019 (CH), 2978 (CH), 2910 (CH), 2801s (CH), 2704, 1613s, 1585, 1467, 1299, 1179, 1154, 1033, 780, 769.

λ_{max} /nm: (acetone) 455 (ϵ /M⁻¹ cm⁻¹ 1200).

Synthesis of [Ni^{II}(OPh)(pyN₂^{Me₂})]Et₄N, tetraethylammonium phenoxo(*N,N'*-bis(2,6-dimethylphenyl)-2,6-pyridinedicarboxamido)nickelate(II), 50a

47 (0.200 g, 0.42 mmol) was dissolved in CH₃OH (3 mL). Et₄NCl.H₂O (0.078 g, 0.42 mmol, 1 eq.) and NaOPh (59 mg, 0.51 mmol, 1.2 eq.) were subsequently added and the solution stirred for 10 minutes. The methanol was removed *in vacuo* and the residue taken up in CH₃CN (3 mL). The dark red solution was filtered, and Et₂O (20 mL) was layered on top of it. Over the course of 5 days, red-brown crystals of the product formed, and were recovered by decanting of the solution (0.186 g, 0.28 mmol, 68%). A crystals suitable for X-ray diffraction was obtained from slow diffusion of Et₂O in DMF solution of the product.

δ H (400 MHz, CDCl₃): 7.86 (1H, t, J = 7.7 Hz, 4-py), 7.56 (1H, d, J = 7.7 Hz, 3,5-py), 7.10 (1H t, J = 7.8 Hz, PhO), 6.87 (1H, t, J = 5.5 Hz, PhO), 6.74–6.67 (7H, s, ArH), 6.52 (1H, t, J = 7.7 Hz, PhO), 6.13 (1H, t, J = 7.0 Hz, PhO), 2.57 (8H, q, J = 7.2 Hz, NCH₂CH₃), 2.50 (12H, s, ArCH₃), 0.88 (12H, t, J = 7.2 Hz, NCH₂CH₃).

δ C (101 MHz, CDCl₃): 167.6 (NC=O), 152.2 (pyridine CH), 144.4 (aniline C_q), 138.4 (pyridine C_q), 134.8 (aniline C_q), 127.3 (CH), 127.1 (CH), 126.8 (aniline CH), 123.3 (aniline CH), 121.8 (pyridine CH), 121.2 (CH), 52.0 (NCH₂CH₃), 19.3 (ArCH₃), 7.3 (NCH₂CH₃).

ESI-MS (m/z): Found: -521.9192 ([Ni(OPh)(pyN₂^{Me₂})]⁻, C₂₉H₂₆N₃NiO₃ requires 522.1328).

ν_{max} (ATR-FTIR) /cm⁻¹: 3060 (CH), 2980 (CH), 2914 (CH), 2850 (CH), 1605s, 1579s, 1478s, 1370, 1295, 1620s, 1608, 1585, 1474, 1430, 1370s, 1295, 833, 755, 681.

λ_{max} /nm: (acetone) 390 (ϵ /M⁻¹ cm⁻¹ 4400), 460sh (850), 530sh (380).

Synthesis of $[\text{Ni}^{\text{II}}(\text{acac})(\text{pyN}_2^{\text{Me}_2})]\text{Et}_4\text{N}$, tetraethylammonium acetylacetonato(*N,N'*-bis(2,6-dimethylphenyl)-2,6-pyridinedicarboxamido)nickelate(II), **51a**

Sodium acetylacetonate ($\text{Na}(\text{acac})$) was obtained by the reaction of equimolar acetylacetone and NaOH in water. After evaporation of the water, the solid residue was washed with acetone and dried *in vacuo* at 120 °C for 6 hours.

In a Schlenk tube, under Ar atmosphere, **48** (0.380 g, 0.64 mmol) was dissolved in anhydrous DMF (4 mL). $\text{Na}(\text{acac})$ (0.082 g, 0.67 mmol, 1.05 eq.) was subsequently added and the solution heated to 60 °C and stirred for 1 hour. The solution was filtered by cannula transfer, concentrated *in vacuo* and finally anhydrous Et_2O (20 mL) was added, causing the formation of dark brown precipitate. The material was redissolved in anhydrous CH_3CN and Et_2O (20 mL) was layered on top of the solution. Over the course of 7 days, blocky brown crystals of the product formed, and were recovered by decanting of the solution (0.210 g, 0.35 mmol, 55%). Crystals suitable for X-ray diffraction were identified in the product. Cocrystals of **51a** and **45a** were obtained from crystallisation of the crude product from wet CH_3CN and Et_2O .

δH (400 MHz, $[\text{D}_6]\text{DMSO}$): 78.8 (2H, 3,4-py), 13.8 (4H, *ArH*), 9.3 (12H, *ArCH*₃), 2.6 (*NCH*₂*CH*₃), 1.1, 0.6 (*NCH*₂*CH*₃), -10.9 (2H, *ArH*), -20.3 (1H, *COCHCO*).

ESI-MS (*m/z*): Found: -528.1426 ($[\text{Ni}(\text{acac})(\text{pyN}_2^{\text{Me}_2})]^-$, $\text{C}_{28}\text{H}_{28}\text{N}_3\text{NiO}_4$ requires 528.1439).

ν_{max} (ATR-FTIR) / cm^{-1} : 3066 (CH), 2982 (CH), 2952 (CH), 2919 (CH), 2855 (CH), 1598, 1561s, 1513, 1465, 1430, 1398, 1368s, 1300, 1261, 1184, 1074, 1015, 924, 907, 759s.

λ_{max} /nm: (acetone) 380sh (ϵ / $\text{M}^{-1}\text{cm}^{-1}$ 1800), 500sh (300), 770 (110), 980 (130).

μ_{eff} / μ_{B} (CD_3CN): 2.99.

Synthesis of $[\text{Ni}^{\text{II}}(\text{bpy})(\text{pyN}_2^{\text{Me}_2})]$, (2,2'-bipyridine)(*N,N'*-bis(2,6-dimethylphenyl)-2,6-pyridinedicarboxamido)nickel(II), **52a**

47 (0.250 g, 0.53 mmol) was dissolved in CH_3CN (5 mL). 2,2'-bipyridine (0.083 g, 0.53 mmol, 1. eq.) was subsequently added and the solution stirred for 10 minutes, causing complete dissolution and formation of a brown colour. Stirring was ceased and Et_2O (20 mL) was layered on top of the solution. Over the course of 4 days, dark brown of the product formed, and were recovered by decanting of the solution (0.240 g, 0.41 mmol, 78%).

δH (400 MHz, CD_3CN): 131.5 (bpy), 64.5 (2H, 3,4-py), 41.5 (2H, bpy). 36.0 (2H, bpy), 14.7 (2H, bpy), 12.2 (4H, 3,5-*ArH*), 6.3 (12H, *ArCH*₃), -6.2 (2H, 4-*ArH*).

ESI-MS (m/z): Found: 586.1761 ($[M + H]^+$, $C_{33}H_{30}N_5NiO_2$ requires 586.1747).

ν_{max} (ATR-FTIR) $/cm^{-1}$: 3056 (CH), 2988 (CH), 2972 (CH), 2901 (CH), 1618, 1599s, 1573s, 1472, 1436, 1366, 1348, 1066s, 760s, 727, 690, 676.

λ_{max} /nm: (acetone) 380sh ($\epsilon /M^{-1} cm^{-1}$ 2400), 470sh (450) 850 (40).

$\mu_{eff.} / \mu_B$ ($CDCl_3$): 2.50.

Synthesis of $[Ni^{II}(terpy)(pyN_2^{Me_2})]$, (2,2';6',2''-terpyridine)(N,N' -bis(2,6-dimethylphenyl)-2,6-pyridinedicarboxamido)nickel(II), 53a

47 (0.110 g, 0.23 mmol) was dissolved in CH_3OH (3 mL). 2,2';6',2''-terpyridine (0.054 g, 0.23 mmol, 1 eq.) was subsequently added and the solution stirred for 10 minutes. Stirring was ceased and Et_2O (20 mL) was layered on top of the solution. Over the course of 3 days, dark brown, microcrystalline product formed, and was recovered by filtration and washed with acetone and diethylether (0.115 g, 0.17 mmol, 75%). Crystals suitable for X-ray diffraction were obtained by repeating the same crystallisation procedure with CH_3OH and Et_2O .

δH (400 MHz, CD_3OD): 28.3, 76.5, 73.7, 72.6, 70.4, 69.6, 44.6, 44.2, 23.1, 22.8, 21.5, 19.0, 17.0, 16.0, 4.5, -7.9, -8.9.

ESI-MS (m/z): Found: 663.2024 ($[M + H]^+$, $C_{38}H_{33}N_6NiO_2$ requires 663.2013).

ν_{max} (ATR-FTIR) $/cm^{-1}$: 3059 (CH), 2998 (CH), 2970 (CH), 2911 (CH), 1611, 1595, 1559s, 1349, 1290, 1062, 769s, 761s, 727, 692, 670, 638.

λ_{max} /nm: (CH_3OH) 440sh ($\epsilon /M^{-1} cm^{-1}$ 70), 860 (100).

$\mu_{eff.} / \mu_B$ (CD_3OD): 3.07.

Synthesis of $[Ni^{II}(2,6-dipic)(pyN_2^{Me_2})]Li_2$, lithium (pyridine-2,6-dicarboxylate)(N,N' -bis(2,6-dimethylphenyl)-2,6-pyridinedicarboxamido)nickelate(II), 54a

Lithium pyridine-2,6-dicarboxylate ($Li_2(2,6-dipic)$) was prepared by the reaction of $LiOH$ and pyridine-2,6-dicarboxylic acid in water, followed by precipitation with acetone and drying under vacuum.

47 (0.207 g, 0.44 mmol) was dissolved in CH_3OH (3 mL). $Li_2(2,6-dipic)$ (0.087 g, 0.53 mmol, 1.2 eq.) was dissolved in 0.5 mL of water, and added to the solution of **47**. The mixture turned light brown and the solvent was immediately evaporated. The residue was washed with ethyl acetate, leaving behind a pistachio-coloured powder. This powder was

redissolved in CH₃OH (2 mL), and methyl-*tert*-butylether (18 mL) was layered on top of the solution. Over the course of 4 days, crystals of the product formed (0.171 g, 0.28 mmol, 64%). Crystals suitable for X-ray diffraction were identified in the product. The crystals presented green and light orange dichroism.

δ H (400 MHz, [D₆]DMSO): 71.3 (2H, 3,5-py), 58.8 (2H, 3,5-py'), 21.6 (1H, 4-py), 19.0 (1H, 4-py'), 14.3 (4H, 3,5-ArH), 10.3 (12H, ArCH₃), -10.1 (2H, 4-ArH).

ESI-MS (*m/z*): Found: -595.1193 ([Ni(2,6-dipic)(HpyN₂^{Me₂})]⁻, C₃₀H₂₅N₄NiO₆ requires 595.1128).

ν_{max} (ATR-FTIR) /cm⁻¹: 3076 (CH), 2927 (CH), 2819 (CH), 2901 (CH), 1606s, 1570, 1560s, 1553, 1465, 1430, 1370s, 1287, 1076, 761.

λ_{max} /nm: (CH₃OH/acetone) 400sh (ϵ /M⁻¹ cm⁻¹ 40), 900 (20).

μ_{eff} / μ_B ([D₆]DMSO): 3.04.

Synthesis of [Ni^{II}(2,6-dipic)]Li₂, lithium bis(pyridine-2,6-dicarboxylate)nickelate(II), 55

54a was dissolved in methanol and toluene, and the resulting solution left to evaporate for 7 days. A few colourless crystals were recovered by decanting the supernatant solution and washed with diethylether. The ¹H NMR and XRD structure parameters correspond to those of previously reported compounds of the [Ni^{II}(2,6-dipic)]²⁻ anion.^{10,18}

δ H (400 MHz, [D₆]DMSO): 62.6 (4H, 3,5-py), 22.0 (2H, 4-py).

Preparation of [Ni^{III}(Cl)(pyN₂^{Me₂})], chloro(*N,N'*-bis(2,6-dimethylphenyl)-2,6-pyridine-dicarboxamido)nickel(III), 48b; [Ni^{III}(OCHO)(pyN₂^{Me₂})], formato(*N,N'*-bis(2,6-dimethylphenyl)-2,6-pyridinedicarboxamido)nickel(III), 49b; and [Ni^{III}(acac)(pyN₂^{Me₂})], acetylacetonato(*N,N'*-bis(2,6-dimethylphenyl)-2,6-pyridinedicarboxamido)nickel(III), 51b

2 mL of a 0.4 mM acetone solution of Ni^{II} precursor (**48a**, **49a**, or **51a**) were cooled to -80 °C in a cuvette. 53 μ L of a freshly prepared 15 mM solution of tris(4-bromophenyl)-ammoniumyl hexachloroantimonate (magic blue, 1 eq.) in acetonitrile were added under continuous stirring. The formation of the Ni^{III} intermediate was immediate as evidenced by the formation of new electronic absorption bands (at 600 nm for **48b**, 530 and 830 nm for **49b**, 530 nm with a shoulder at 720 nm for **51b**).

Preparation of $[\text{Ni}^{\text{III}}(\text{bpy})(\text{pyN}_2^{\text{Me}_2})]^+$, (2,2'-bipyridine)(*N,N'*-bis(2,6-dimethylphenyl)-2,6-pyridinedicarboxamido)nickel(III), 52b

2 mL of a 0.4 mM solution of **52a** (in 9/1 acetone/acetonitrile) were cooled to -80 °C in a cuvette. 40 µL of a freshly prepared 0.05 M solution of cerium ammonium nitrate in acetonitrile (2 eq.) were added under continuous stirring. A new band at 580 nm, with a shoulder at 790 nanometres, slowly appeared over the course of 50 minutes.

Preparation of $[\text{Ni}^{\text{III}}(\text{terpy})(\text{pyN}_2^{\text{Me}_2})]^+$, (2,2';6',2''-terpyridine)(*N,N'*-bis(2,6-dimethylphenyl)-2,6-pyridinedicarboxamido)nickel(III), 53b

2 mL of a 0.4 mM methanolic solution of **53a** were cooled to the desired temperature (-80 °C < *T* < -40 °C) in a cuvette. 40 µL of a freshly prepared 0.04 M solution of cerium ammonium nitrate in acetonitrile (2 eq.) were added under continuous stirring. Bands at 420 nm, 500 nm and 680 nm appeared over the course of 200 s (at -80 °C), evidencing the formation of **53b**.

Preparation of $[\text{Ni}^{\text{III}}(2,6\text{-dipic})(\text{pyN}_2^{\text{Me}_2})]^-$, (pyridine-2,6-dicarboxylate)(*N,N'*-bis(2,6-dimethylphenyl)-2,6-pyridinedicarboxamido)nickelate(III), 54b

2 mL of a 0.4 mM solution of **54a** in 1/1 CH₃OH/acetone were cooled to the desired temperature (-80 °C < *T* < -40 °C) in a cuvette. 40 µL of a freshly prepared 0.04 M solution of cerium ammonium nitrate in acetonitrile (2 eq.) were added under continuous stirring. A broad band at 560 nm, with a shoulder at 700 nm, appeared over the course of 20 s (at -40 °C), evidencing the formation of **53b**.

X-Ray diffraction methods

Single crystal X-ray data were collected at 100(2) K on a Bruker Apex II CCD diffractometer using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å), an Oxford Cryo-systems Cobra low temperature device and a MiTeGen micromount. Bruker APEX¹⁹ software was used to correct for Lorentz and polarization effects. The structures were solved and refined using the Bruker SHELXTL Software Package.^{20,21}

X-ray structure refinement notes

The structure of **50a** contains one molecule of DMF in the asymmetric unit. The asymmetric unit of the cocrystal **51a.45a** contains one molecule of **51a**, one of **45a** and two molecules of water. One of the two NEt₄ groups is disordered and was modelled with constraints (EADP) in two positions with occupancies of 60:40%. The structure of **51a** contains no solvents of crystallisation. The structure of **52a** contains two distinct molecules of **52a**. Two dimethylphenyl rings are disordered in two positions with occupancy 75:25%. A rigid model was used to refine the lower occupancy part. Restraints (SADI) and constraints (EADP) were used to model this. There is also approx. 10% MeCN coordinating to one of the two Ni centres. This was modelled with restraints (ISOR). The structure was modelled as an inversion twin with a Flack parameter of 0.385(9). In **54a**, one dimethylphenyl pendant group is disordered in two positions with 55:45% occupancy and modelled with restraints (SADI) and constraints (EADP). The Li₂ cation are coordinated by solvents (CH₃OH and H₂O); one CH₃OH and one water are disordered in two positions (80:20% occupancy) and were modelled with restraints and constraints (SADI, ISOR and EADP).

Table 4.3. Crystal data and structure refinement parameters for **50a**, **51a**, and **51a.45a**.

	50a	51a	51a.45a
Empirical formula	C ₄₀ H ₅₃ N ₅ NiO ₄	C ₃₆ H ₄₈ N ₄ NiO ₄	C ₆₉ H ₉₆ N ₈ Ni ₂ O ₁₀
Formula weight	726.58	659.49	1314.95
Temperature	100(2) K	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Triclinic	Orthorhombic
Space group	Cc	P $\bar{1}$	Pca2 ₁
Unit cell dimensions	$a = 10.7254(3)$ Å $\alpha = 90^\circ$ $b = 25.8288(7)$ Å $\beta = 98.2736(9)^\circ$ $c = 14.2807(4)$ Å $\gamma = 90^\circ$	$a = 11.0309(4)$ Å $\alpha = 96.3180(10)^\circ$ $b = 11.2311(4)$ Å $\beta = 108.0980(10)^\circ$ $c = 14.6563(5)$ Å $\gamma = 95.890(2)^\circ$	$a = 27.2970(16)$ Å $\alpha = 90^\circ$ $b = 14.8930(9)$ Å $\beta = 90^\circ$ $c = 16.7320(10)$ Å $\gamma = 90^\circ$
Volume	3914.92(19) Å ³	1697.36(10) Å ³	6802.1(7) Å ³
Z	4	2	4
Density (calculated)	1.233 Mg/m ³	1.290 Mg/m ³	1.284 Mg/m ³
Absorption coefficient	0.541 mm ⁻¹	0.615 mm ⁻¹	0.616 mm ⁻¹
F(000)	1552	704	2808
Crystal size	0.170 x 0.170 x 0.100 mm ³	0.22 x 0.22 x 0.19 mm ³	0.27 x 0.15 x 0.13 mm ³
Theta range for data collection	1.577 to 27.936°	2.817 to 28.499°	2.362 to 28.348°
Index ranges	$-14 \leq h \leq 14$, $-34 \leq k \leq 34$, $-18 \leq l \leq 18$	$-14 \leq h \leq 14$, $-15 \leq k \leq 15$, $-19 \leq l \leq 19$	$-36 \leq h \leq 28$, $-19 \leq k \leq 14$, $-22 \leq l \leq 22$
Reflections collected	75208	72445	49754
Independent reflections	8876 [R(int) = 0.0350]	8549 [R(int) = 0.0539]	16869 [R(int) = 0.0856]
Completeness to theta=	25.242° 100.0 %	26.000° 99.9 %	26.000° 99.8 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.7016	0.7457 and 0.6901	0.7457 and 0.6914
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	8876 / 20 / 461	8549 / 0 / 416	16869 / 5 / 816
Goodness-of-fit on F ²	1.015	1.038	1.018
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0290, wR2 = 0.0676	R1 = 0.0348, wR2 = 0.0726	R1 = 0.0585, wR2 = 0.1095
R indices (all data)	R1 = 0.0352, wR2 = 0.0704	R1 = 0.0486, wR2 = 0.0774	R1 = 0.1061, wR2 = 0.1257
Largest diff. peak and hole	0.482 and -0.229 e Å ⁻³	0.391 and -0.449 e Å ⁻³	0.629 and -0.436 e Å ⁻³

Table 4.4. Crystal data and structure refinement parameters for **52a**, **53a**, **54a** and **55**.

	52a	53a	54a	55
Empirical formula	C _{33.10} H _{29.15} N _{5.05} NiO ₂	C ₃₈ H ₃₂ N ₆ NiO ₂	C ₃₆ H ₅₀ Li ₂ N ₄ NiO ₁₃	C ₁₆ H ₁₈ Li ₂ N ₂ NiO ₁₂
Formula weight	588.37	663.40	819.39	502.91
Temperature	100(2) K	100(2) K	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	P2 ₁	Pbca	P2 ₁ /c	P2 ₁ /n
Unit cell dimensions	<i>a</i> = 12.9031(11) Å <i>α</i> = 90° <i>b</i> = 14.7169(14) Å <i>β</i> = 92.539(3)° <i>c</i> = 15.5333(13) Å <i>γ</i> = 90°	<i>a</i> = 15.6038(6) Å <i>α</i> = 90° <i>b</i> = 15.6097(7) Å <i>β</i> = 90° <i>c</i> = 25.1195(10) Å <i>γ</i> = 90°	<i>a</i> = 13.0215(9) Å <i>α</i> = 90° <i>b</i> = 31.5481(19) Å <i>β</i> = 113.689(2)° <i>c</i> = 11.2308(7) Å <i>γ</i> = 90°	<i>a</i> = 9.9189(6) Å <i>α</i> = 90° <i>b</i> = 20.9731(10) Å <i>β</i> = 106.185(2)° <i>c</i> = 10.0860(5) Å <i>γ</i> = 90°
Volume	2946.8(5) Å ³	6118.4(4) Å ³	4224.9(5) Å ³	2015.03(19) Å ³
Z	4	8	4	4
Density (calculated)	1.326 Mg/m ³	1.440 Mg/m ³	1.288 Mg/m ³	1.658 Mg/m ³
Absorption coefficient	0.697 mm ⁻¹	0.681 mm ⁻¹	0.523 mm ⁻¹	1.032 mm ⁻¹
F(000)	1228	2768	1728	1032
Crystal size	0.41 x 0.22 x 0.12 mm ³	0.16 x 0.15 x 0.1 mm ³	0.27 x 0.14 x 0.07 mm ³	0.18 x 0.11 x 0.03 mm ³
Theta range for data collection	2.625 to 28.778°	2.611 to 26.808°	2.582 to 26.193°	1.942 to 26.056°
Index ranges	-17 ≤ <i>h</i> ≤ 17, -19 ≤ <i>k</i> ≤ 19, -21 ≤ <i>l</i> ≤ 21	-14 ≤ <i>h</i> ≤ 19, -19 ≤ <i>k</i> ≤ 19, -31 ≤ <i>l</i> ≤ 28	-16 ≤ <i>h</i> ≤ 15, -39 ≤ <i>k</i> ≤ 36, -13 ≤ <i>l</i> ≤ 13	-12 ≤ <i>h</i> ≤ 12, -25 ≤ <i>k</i> ≤ 25, -12 ≤ <i>l</i> ≤ 12
Reflections collected	61082	95924	54805	51839
Independent reflections	15266 [R(int) = 0.0492]	6527 [R(int) = 0.0829]	8438 [R(int) = 0.0696]	3982 [R(int) = 0.0963]
Completeness to theta=	26.000° 99.9 %	25.242° 99.9 %	25.242° 99.9 %	25.242° 100.0 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.7458 and 0.6592	0.7454 and 0.7061	0.7453 and 0.6264	0.7453 and 0.6605
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	15266 / 21 / 721	6527 / 0 / 428	8438 / 33 / 546	3982 / 6 / 324
Goodness-of-fit on F ²	1.032	1.027	1.144	1.068
Final R indices [<i>I</i> > 2σ(<i>I</i>)]	R1 = 0.0346, wR2 = 0.0715	R1 = 0.0381, wR2 = 0.0738	R1 = 0.0811, wR2 = 0.1882	R1 = 0.0398, wR2 = 0.0713
R indices (all data)	R1 = 0.0469, wR2 = 0.0770	R1 = 0.0640, wR2 = 0.0825	R1 = 0.1011, wR2 = 0.1981	R1 = 0.0654, wR2 = 0.0780
Largest diff. peak and hole	0.434 and -0.381 e Å ⁻³	0.341 and -0.384 e Å ⁻³	1.104 and -0.647 e Å ⁻³	0.375 and -0.483 e Å ⁻³

Cyclic voltammetry

CV experiments were conducted on 1 mM solutions of compounds **47** and **48-54a**, at room temperature, with a 0.05 V s⁻¹ scan rate. The solvents were acetone, or acetone/acetonitrile (for compound **52a**) or acetone/methanol (for compounds **53a** and **54a**) mixtures. The supporting electrolyte was 0.1 M Bu₄NPF₆. Potentials were referenced to the Fc⁺/Fc couple by addition of an internal ferrocene standard to the solutions. Performing the measurements in air or in an inert Ar atmosphere did not sort appreciable differences. All solutions, except for **50a**, showed one (quasi)reversible redox wave between -2 and 0.5 V, in the steady state. Scanning to more extreme potentials (up to 1.4 V) caused rapid fouling of the electrode surface with progressively diminishing currents over successive scans, only remedied by interrupting the experiment and polishing the electrode.

EPR

EPR samples were prepared by freezing solutions of **48-54b**, prepared according to the above procedures, in EPR tubes in liquid nitrogen. The EPR spectra were recorded at 77 K, 9.2 GHz, 2 mW microwave power, with a 100 mT field sweep in 84 s, and 0.5 mT, 100 kHz field modulation. Integration, simulation, and fitting were executed with Matlab and the easySpin computational package.²² Quantification of the concentration of spins in the samples was obtained by comparison of the double integral of the signals to that of a frozen 0.5 mM acetone solution of TEMPO, measured under the same conditions. The concentrations thus determined, together with the electronic absorption spectroscopy absorbance values for the same samples, were used to calculate the absorptivities of **48-54b** via the Beer-Lambert law. The systems were modelled as the powder patterns of S = ½ electron spin systems with anisotropic g tensor with inhomogeneous line broadening (fig. 4.6). Hyperfine coupling to one ^{35/37}Cl (*I* = 3/2) nucleus for **48b**, one ¹⁴N (*I* = 1) for **52b**, and two ¹⁴N for **53b** was included in the simulations, with *A_{zz}* as the only non-zero component of the coupling constant.

Reactivity studies

General procedure for reactivity experiments

Solutions of the nickel(III) compounds were prepared according to the methods described above for the reactivity studies with 2,6-DTBP. **51-54b** were tested at -40 °C; **54b** was also reacted after warming to 25 °C. 2,6-DTBP was added as a 1 M acetone solution.

The consumption of the nickel(III) compounds was monitored using electronic absorption spectroscopy, by observing the disappearance of their characteristic visible/NIR features over time.

Rate constants determination

Rate constants were determined for the reactions of **52b** and **53b** with 2,6-DTBP, at -40 °C. A minimum of 10 equivalents of substrate were used to ensure pseudo-first order conditions. The second-order rate constants (k_2) were determined from the linear dependence of the pseudo-first order constants (k_{obs}) on substrate concentration. Values for the observed k_{obs} were obtained by fitting the decay of the absorbance at 580 nm (**52b**) or 680 nm (**53b**) as an exponential. Each experiment was repeated three times, and the average k_{obs} value was utilized for the determination of k_2 .

References

- (1) Huang, D.; Holm, R. H. *J. Am. Chem. Soc.* **2010**, *132*, 4693–4701.
- (2) Allpress, C. J.; Berreau, L. M. *Eur. J. Inorg. Chem.* **2014**, 4642–4649.
- (3) Allpress, C. J.; Arif, A. M.; Houghton, D. T.; Berreau, L. M. *Chem. Eur. J.* **2011**, *17*, 14962–14973.
- (4) Berreau, L. M.; Borowski, T.; Grubel, K.; Allpress, C. J.; Wikstrom, J. P.; Germain, M. E.; Rybak-Akimova, E. V.; Tierney, D. L. *Inorg. Chem.* **2011**, *50*, 1047–1057.
- (5) Dai, Y.; Wensink, P. C.; Abeles, R. H.; Robert, H. *J. Biol. Chem.* **1999**, *274*, 1193–1195.
- (6) Yang, L.; Powell, D. R.; Houser, R. P. *Dalton Trans.* **2007**, 955–964.
- (7) Addison, C. C.; Gatehouse, B. M. *J. Chem. Soc.* **1960**, 613–616.
- (8) Alvarez, S.; Avnir, D.; Llunell, M.; Pinsky, M. *New J. Chem.* **2002**, *26*, 996–1009.
- (9) Belle, C.; Bougault, C.; Averbuch, M.-T.; Durif, A.; Pierre, J.-L.; Latour, J.-M.; Le Pape, L. *J. Am. Chem. Soc.* **2001**, *123*, 8053–8066.
- (10) Evilia, R. F.; Young, D. C.; Reilley, C. N. *J. Coord. Chem.* **1973**, *3*, 17–25.
- (11) Barefield, E. K.; Busch, D.; Nelson, S. *Q. Rev. Chem. Soc.* **1968**, *22*, 457–498.
- (12) Cotton, A. F.; Wilkinson, G.; Bochmann, M.; Murillo, C. A., *Advanced Inorganic Chemistry*; Wiley: 1999.
- (13) Schultz, M.; Plessow, P.-N.; Rominger, F.; Weigel, L. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2013**, *69*, 1437–1447.
- (14) Haines, R.; McAuley, A. *Coord. Chem. Rev.* **1981**, *39*, 77–119.
- (15) Bryant, J. R.; Mayer, J. M. *J. Am. Chem. Soc.* **2003**, *125*, 10351–10361.
- (16) Evans, D. F.; Jakubovic, D. A. *J. Chem. Soc., Dalton Trans.* **1988**, 2927–2933.
- (17) Bain, G. A.; Berry, J. F. *J. Chem. Educ.* **2008**, *85*, 532–536.
- (18) Xiang, J.; Yin, Y.-G.; Huang, X.-C. *Acta Crystallogr. Sect. E* **2006**, *62*, m213–m215.
- (19) Bruker APEX v2014.11-0, Bruker AXS Inc., Madison, Wisconsin, USA.
- (20) SHELXL-2014, Bruker AXS Inc., Madison, Wisconsin, USA.
- (21) Sheldrick, G. *Acta Crystallogr. Sect. A* **2008**, *64*, 112–122.
- (22) Stoll, S.; Schweiger, A. *J. Magn. Reson.* **2006**, *178*, 42–55.

Chapter 5

Evidence for a Transient High Valent Oxidant in the Reaction of a Nickel(II) Complex with *m*-CPBA

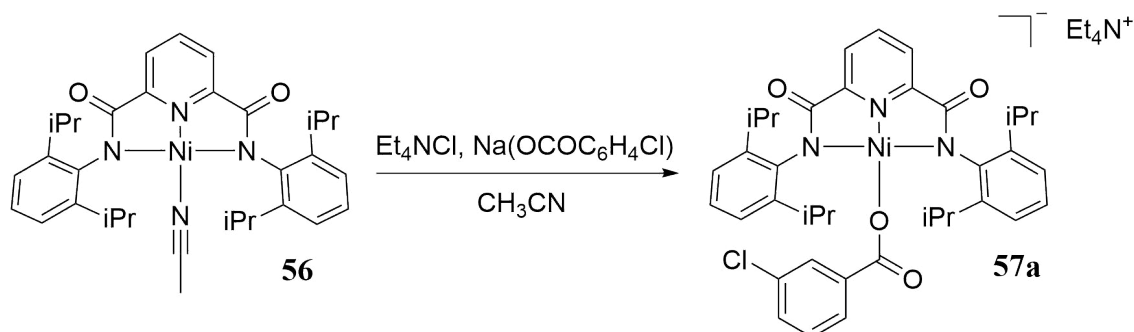
A manuscript detailing the work described in this chapter has been submitted for publication. The DFT calculations were performed by Prof. Marcel Swart (University of Girona, Spain); the XRD data collection and structure solutions and refinements were done by Dr Brendan Twamley (Trinity College Dublin); Prof. Robert Barkley (Trinity College Dublin) provided access and training to the EPR instrument.

5.1 Introduction

The $\text{Ni}^{\text{III}}\text{--O--X}$ species presented in the previous chapter represented a remarkable group of oxidants, that were proficient in hydrogen atom transfer and proton-coupled electron transfer reactions. Nevertheless, Ni=O complexes are more often invoked as the intermediates in catalytic oxidations (section 1.5). For example, early mechanistic studies on Ni-catalysed epoxidation reactions proposed $\text{Ni}^{\text{IV}}\text{=O}$ as an oxidising reagent, on the basis of analysis of product distribution and side reactions.¹ More recently, Itoh and Palaniandavar have demonstrated Ni-catalysed alkane oxidations, and suggested a $\text{Ni}^{\text{II}}\text{--O}^\bullet$ or $\text{Ni}^{\text{III}}\text{=O}$ oxidant.^{2–7} I set out to attempt the preparation of such species by reacting Ni^{II} precursors with oxygen atom transfer reagents. In this chapter, the reaction of a Ni^{II} complex (**56**, sch. 5.1) towards meta-chloroperoxybenzoic acid (*m*-CPBA) is explored, and evidence for the formation of a transient high valent $\text{Ni}^{\text{III}}\text{--O}^\bullet$ oxidant, and thermodynamically more stable $\text{Ni}^{\text{III}}\text{--carboxylate}$ species, is provided.

5.2 Synthesis of a nickel(II) acetonitrile complex and reaction with *m*-CPBA

$[\text{Ni}^{\text{II}}(\text{CH}_3\text{CN})(\text{pyN}_2^{\text{iPr}_2})]$ (**56**, sch. 5.1) was synthesised by deprotonating $\text{H}_2\text{pyN}_2^{\text{iPr}_2}$ with NaH (2 eq.) in THF, and reacting the resulting mixture with $\text{Ni}(\text{OTf})_2$. Work-up and re-crystallisation from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ afforded brown/red crystals of **56**. This replicates the procedure employed for the preparation of $[\text{Ni}^{\text{II}}(\text{CH}_3\text{CN})(\text{pyN}_2^{\text{Me}_2})]$ (**47**, chapter 3). Structural assignment and characterisation were achieved by NMR, FTIR, and electronic absorption spectroscopies and X-ray diffraction of single crystals (fig. 5.1).



Scheme 5.1. Preparation of **57a** by ligand exchange with **56**. $\text{Et}_4\text{N}(\text{OCOC}_6\text{H}_4\text{Cl})$ was generated in situ by metathesis of Et_4NCl and $\text{Na}(\text{OCOC}_6\text{H}_4\text{Cl})$.

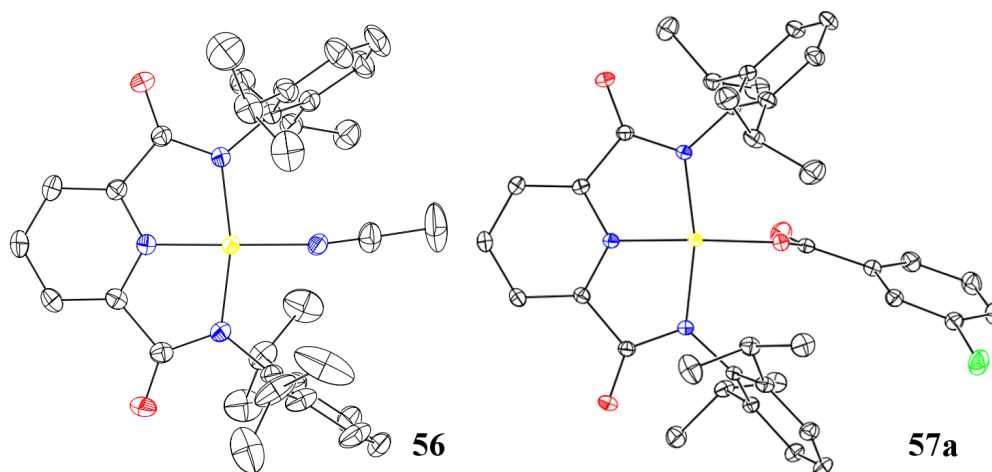


Figure 5.1. ORTEP plots (at 50% probability level) of the X-ray structures of **56** and **57a**. Hydrogen atoms, one molecule of Et₂O in **56**, the Et₄N⁺ counterion and one molecule of CH₃CN in **57a** have been omitted for clarity.

Upon addition of *m*-CPBA (2 equiv.) to a solution of **56** at 25 °C (0.5 mM, 2 mL, acetone or CH₃CN), a colour change from orange to dark purple occurred. The maximum yield of the purple species, on the basis of the intensity of the newly formed electronic absorption bands (λ_{max} = 560 nm, shoulder at 760 nm, fig. 5.2), was obtained after 350 s. The purple species subsequently decayed with a half-life of 2100 s at 25 °C. The previously reported [Ni^{III}(OX)(pyN₂^{Me₂})] (OX = OCO₂H, OAc, and ONO₂) complexes displayed absorption features in the range λ_{max} = 500-900 nm (chapters 2 and 3). The spectrum of the product of the **56** + *m*-CPBA reaction is reminiscent of these compounds, suggesting a [Ni^{III}(OX)(pyN₂^{*i*Pr₂})] species had formed.

ESI-MS analysis of the **56** + *m*-CPBA mixture revealed one peak, with an isotopic pattern typical of a Ni containing species, at m/Z = 696. A [Ni(OCOC₆H₄Cl)(pyN₂^{*i*Pr₂})]⁺ ion (m/Z = 696.2139, fig. 5.4) is consistent with it: presumably this species results from the ionisation of a neutral [Ni^{III}(OCOC₆H₄Cl)(pyN₂^{*i*Pr₂})] species present in solution.

EPR analysis of the reaction mixture (fig. 5.3) displayed a signal suggestive of a mixture of two low-spin $S = \frac{1}{2}$ d^7 Ni^{III} species, similar to previously reported Ni^{III} complexes (chapters 2 and 3). The spectrum was simulated as an approximately 1:1 mixture of an axial signal ($g_{\perp}$ = 2.23, $g_{\parallel}$ = 2.01) $g_{\perp}$, $g_{\parallel}$ and a markedly more rhombic one (g_x = 2.42, g_y = 2.26, g_z = 1.99). Double integration of the signal and comparison with a radical standard (0.5 mM TEMPO) demonstrated a total yield of $S = \frac{1}{2}$ species of $\sim 50\% \pm 20\%$, on the basis of the starting concentration of **56**. On the basis of the electronic absorption, mass, and EPR spectra, and in analogy with previously studied [Ni^{III}(OX)(pyN₂^{Me₂})] complexes, it was suggested that one of the products was [Ni^{III}(OCOC₆H₄Cl)(pyN₂^{*i*Pr₂})] (**57b**).

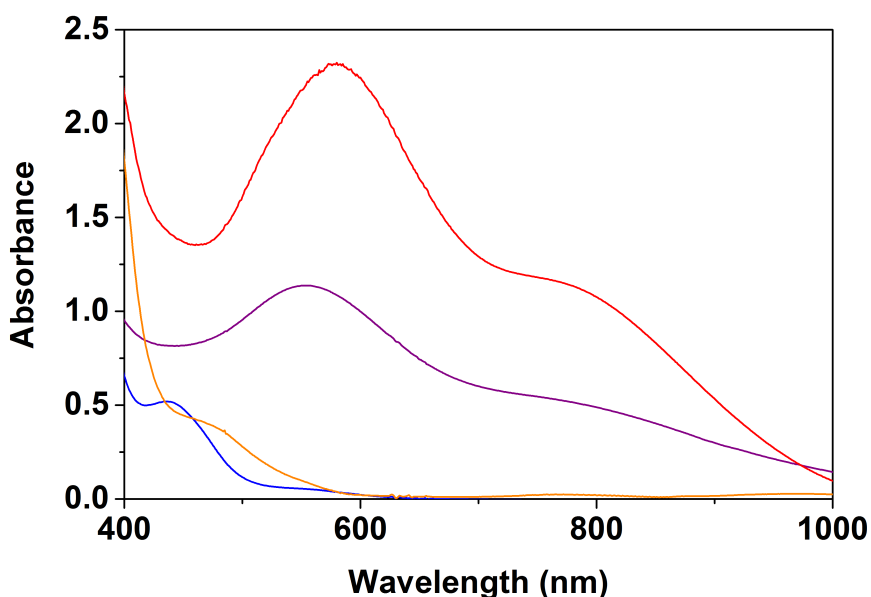


Figure 5.2. Electronic absorption spectra of **56** (0.5 mM, acetone, 25 °C, blue trace) and the same solution after addition of *m*-CPBA (2 equiv., 25 °C, purple trace); **57a** (0.5 mM, acetone, -80 °C, orange trace) and of the oxidation product **57b** resulting from the addition of 1 equiv. magic blue (red trace) to **57a**.

5.3 Synthesis and oxidation of a nickel(II) 3-chlorobenzoate complex

As previously shown, $[\text{Ni}^{\text{III}}(\text{OX})(\text{pyN}_2^{\text{Me}_2})]$ could be prepared by the one electron oxidation of the corresponding $[\text{Ni}^{\text{II}}(\text{OX})(\text{pyN}_2^{\text{Me}_2})]^-$ (chapters 2 and 3). In order to prepare the putative $[\text{Ni}^{\text{III}}(\text{OCOC}_6\text{H}_4\text{Cl})(\text{pyN}_2^{\text{iPr}_2})]$ (**57b**), the corresponding Ni^{II} complex was synthesised. $\text{Et}_4\text{N}[\text{Ni}^{\text{II}}(\text{OCOC}_6\text{H}_4\text{Cl})(\text{pyN}_2^{\text{iPr}_2})]$, **57a** (sch. 5.1) was obtained by the reaction of **56** with crude $\text{Et}_4\text{N}(\text{OCOC}_6\text{H}_4\text{Cl})$ (obtained by the metathesis of Et_4NCl and $\text{Na}(\text{OCOC}_6\text{H}_4\text{Cl})$ in CH_3OH). Single crystal X-ray diffraction measurements confirmed the structure of **57a** (fig. 5.1), and was supported by NMR, FTIR, and ESI-MS.

The oxidation of **57a** with tris(3-bromophenyl)ammoniumyl hexachloroantimonate (magic blue, 1 equiv., -80 °C, acetone) resulted in a purple solution, whose electronic absorption spectrum displayed bands at $\lambda_{\text{max}} = 580$ and 780 (shoulder) nm (fig. 5.2). Such features have been identified as typical for $[\text{Ni}^{\text{III}}(\text{OX})(\text{pyN}_2^{\text{Me}_2})]$ complexes (chapter 3), allowing to identify this compound as $[\text{Ni}^{\text{III}}(\text{OCOC}_6\text{H}_4\text{Cl})(\text{pyN}_2^{\text{iPr}_2})]$ (**57b**). Critically, the obtained spectrum possessed a similar profile to that obtained from the **56** + *m*-CPBA mixture, with intense bands in the visible region (fig. 5.2, fig. A.100). However, there was a shift in the

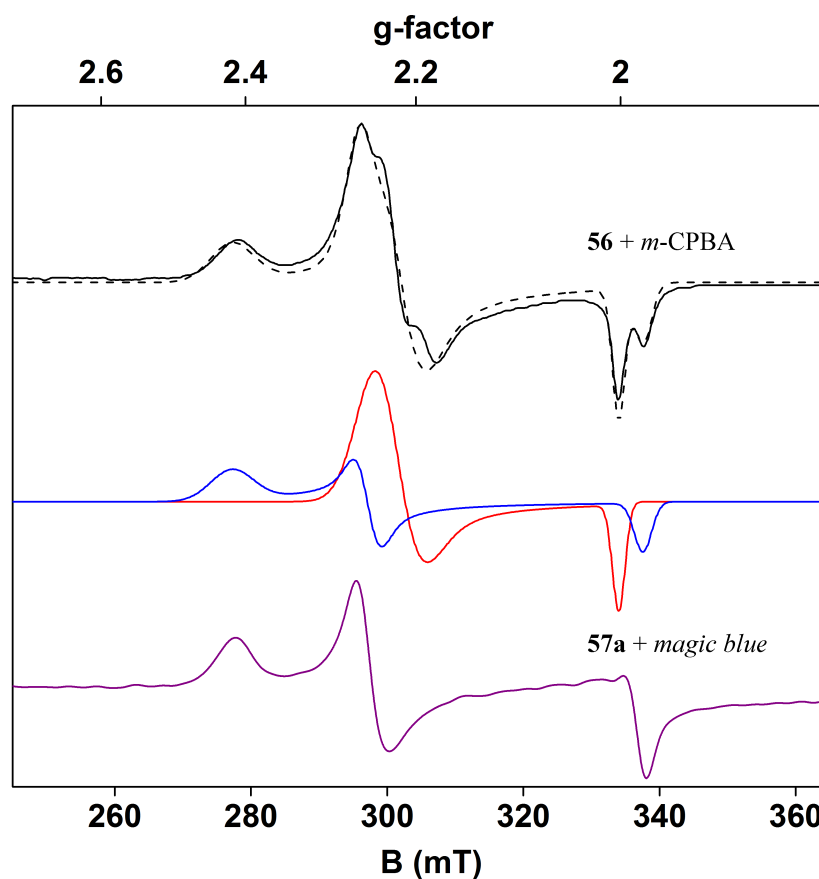


Figure 5.3. X-Band EPR spectra of the reaction mixture of **56** and *m*-CPBA (top, black line; dashed line = simulated spectrum) and of **57a** and magic blue (purple, bottom); measured at 77 K in frozen acetone solution, 2 mW microwave power. Simulated spectra (middle) of the two individual components of the **56** + *m*-CPBA mixture are in red ($g_{\perp} = 2.23$, $g_{\parallel} = 2.01$) and blue ($g_x = 2.42$, $g_y = 2.26$, $g_z = 1.99$).

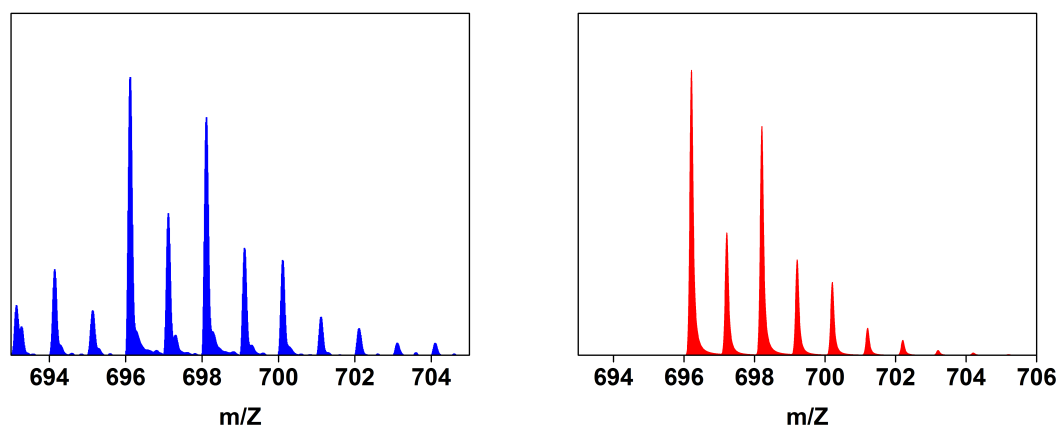


Figure 5.4. Positive mode ESI-MS of the mixture of **56** + *m*-CPBA (blue, left); simulation of the ion **57⁺** ($\text{C}_{38}\text{H}_{41}\text{ClN}_3\text{NiO}_4$, $m/Z = 696.2139$, red, right).

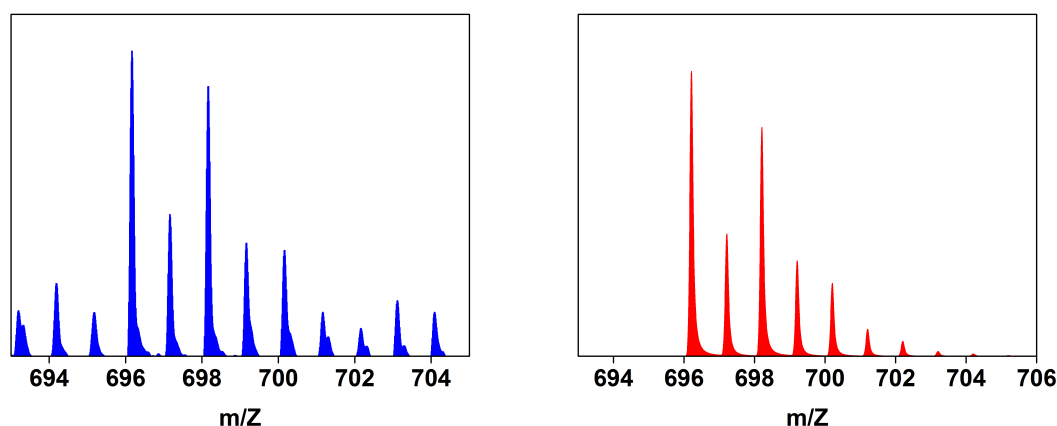


Figure 5.5. Positive mode ESI-MS of the mixture of **57a** + magic blue (blue, left); simulation of the ion **57⁺** ($\text{C}_{38}\text{H}_{41}\text{ClN}_3\text{NiO}_4$, $m/Z = 696.2139$, red, right).

λ_{max} values (20 nm), which can be ascribed to the presence of at least two Ni^{III} species in the **56** + *m*-CPBA reaction mixture.

The EPR spectrum of **57b** (figs. 5.3 and A.101) corresponded to a single species ($g_x = 2.42$, $g_y = 2.26$, $g_z = 1.99$). Such signals are typical of $[\text{Ni}^{\text{III}}(\text{OX})(\text{pyN}_2^{\text{R}_2})]$ species (chapters 2 and 3). Importantly, **57b** displayed EPR features identical to the rhombic component in the mixture obtained from the mixture of **56** and *m*-CPBA (fig. 5.3).

ESI-MS analysis of pure **57b** showed a peak at $m/Z = 696$, corresponding to a **57⁺** ion, which was also observed in the **56** + *m*-CPBA mixture (fig. 5.5). The same product (**57b**, $[\text{Ni}^{\text{III}}(\text{OCOC}_6\text{H}_4\text{Cl})(\text{pyN}_2^{\text{iPr}_2})]$) was thus obtained from the one-electron oxidation of **57a**, as from the reaction of **56** with excess *m*-CPBA.

5.4 Analysis of decay products

The formation of **57b** corresponds to a net one-electron oxidation of **56**. *m*-CPBA can react either as a two- or one-electron oxidant. Two-electron oxidation by *m*-CPBA results from heterolytic O–O bond scission, while a one-electron oxidation derives from homolytic O–O bond scission.

It has been previously reported that these two occurrences can be distinguished on the basis of the *m*-CPBA-derived products.^{7–10} In the former a $\text{Ni}^{\text{IV}}=\text{O}/\text{Ni}^{\text{III}}-\text{O}^\bullet$ moiety and meta-chlorobenzoic acid (*m*-CBA) would form and in the latter a $\text{Ni}^{\text{III}}=\text{O}/\text{Ni}^{\text{II}}-\text{O}^\bullet$ entity and a meta-chlorobenzene carboxyl radical would form. The meta-chlorobenzene carboxyl radical would decay further by decarboxylation and further radical-type reactions to yield chlorobenzene, 1,3-dichlorobenzene, or 3-chlorophenol.¹⁰

The **56** + *m*-CPBA reaction mixture was analysed by GC-MS, after acidic work-up, but didn't identify any of chlorobenzene, 1,3-dichlorobenzene, or 3-chlorophenol. Moreover, separation by column chromatography of the post-reaction mixture showed recovery of *m*-CBA in high yield (>90%). These observations suggest that the reaction of **56** with *m*-CPBA resulted in heterolytic cleavage of the O–O bond, and the formation of a $\text{Ni}^{\text{IV}}=\text{O}/\text{Ni}^{\text{III}}-\text{O}^\bullet$ species. **57b** is not a $\text{Ni}^{\text{IV}}=\text{O}/\text{Ni}^{\text{III}}-\text{O}^\bullet$ complex, and therefore, one can assume it derives from the transient $\text{Ni}^{\text{IV}}=\text{O}/\text{Ni}^{\text{III}}-\text{O}^\bullet$ species (sch. 5.3), as a result of HAA of solvent by the $\text{Ni}^{\text{IV}}=\text{O}/\text{Ni}^{\text{III}}-\text{O}^\bullet$ and subsequent ligand exchange by *m*-CBA.

Heterolytic O–O bond scission is further corroborated by DFT calculations (S12g / TZ2P // BP86-D3 / TDZP including COSMO solvation and ZORA relativistic effects^{11–15} which showed that after binding of *m*-CPBA, the O–O bond breaks spontaneously resulting in a hydroxo- Ni^{IV} -carboxylate adduct (fig. 5.9). Subsequent loss of *m*-CBA, after proton transfer from this adduct leads to the formation of a $\text{Ni}^{\text{III}}-\text{O}^\bullet$ species (fig. 5.10). The $\text{Ni}^{\text{III}}-\text{O}^\bullet$ entity ($S = 1$) was found to be more stable than the $\text{Ni}^{\text{IV}}=\text{O}$ ($S = 0$) by ca. 9 kcal/mol and carries unpaired spin density on both the metal/nitrogens and the oxygen atoms (fig. 5.11).

5.4.1 Formation of a benzoxazine-containing modified ligand

In order to understand the **56** + *m*-CPBA reaction further, an acidic work-up of the reaction mixture was performed, which caused demetallation, and isolated all organic products by column chromatography. Alongside non-derivatised ligand ($\text{H}_2\text{pyN}_2^{\text{iPr}_2}$) one major ligand-oxidised product (**58**) was obtained (fig. 5.6), as well as traces of other degradation products. Importantly, none of these ligand-derived organic molecules were formed in the reaction of $\text{H}_2\text{pyN}_2^{\text{iPr}_2}$ with *m*-CPBA (room temperature, acetone) in the absence of a metal, or from the natural decay of **57b** (prepared with magic blue in acetone, -45 °C to room temperature). Crystals of **58** that were suitable for X-ray diffraction, obtained from ethanol/ H_2O , demonstrated **58** to be a benzoxazine derivative of $\text{H}_2\text{pyN}_2^{\text{iPr}_2}$ (fig. 5.6). The yield of **58**, after column chromatography, was 35% relative to the quantity of **56**.

There are two plausible mechanisms for the formation of **58** in the reaction of **56** with *m*-CPBA (sch. 5.2). In both cases, the putative $\text{Ni}^{\text{III}}-\text{O}^\bullet$ presumably abstracts a hydrogen atom from a benzylic C–H, yielding a benzylic radical and a $\text{Ni}^{\text{III}}-\text{OH}$. These products could undergo radical rebound to yield a hydroxylated species (mechanism A, sch. 5.2). The hydroxylated ligand could then undergo cyclisation-condensation, to yield the benzoxazine product.

Alternatively, the benzylic radical would react directly with the carboxamide oxygen, in a radical coupling fashion, ultimately yielding the benzoxazine (mechanism B, sch. 5.2).

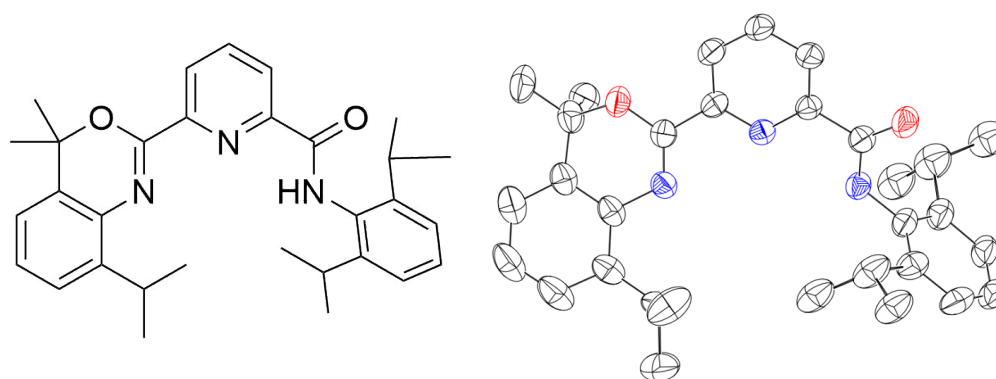
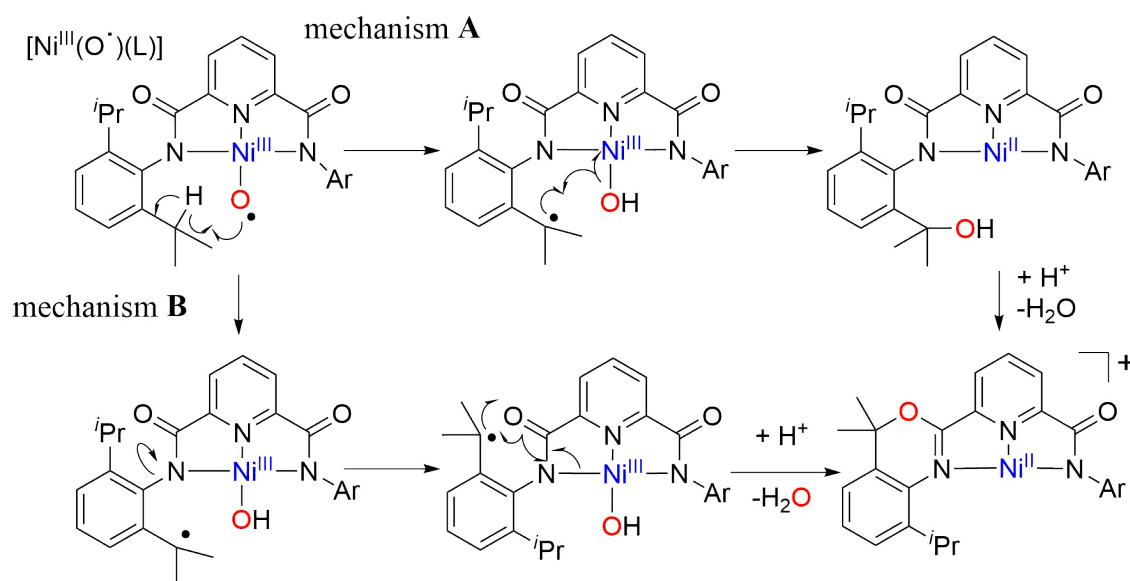


Figure 5.6. Structure of **58** (left), and ORTEP plot (at 50% probability level) of its X-ray structures. Hydrogen atoms and one molecule of EtOH have been omitted for clarity.

Analogous benzo-1,3-oxazines are typically prepared by the cyclisation-condensation of 2-acylamido-benzylalcohols, promoted by acids, thus supporting mechanism A.^{16–18} Metal based oxidants such as MnO₂ or PbO₂ have been observed to effect the transformation of *o*-alkyl-acetanilides to benzoxazines, but the mechanism is unknown.^{19,20} To the extent of my knowledge, radical-type mechanisms (as in mechanism B, sch. 5.2) have not been investigated.



Scheme 5.2. Possible mechanisms for the formation of benzo-1,3-oxazine **58**.

The two mechanisms can be differentiated by the source of the oxygen atom in the product: the putative Ni^{III}–O[•] oxidant in case A, or the carboxamide O-atom originally present in the ligand in case B. In order to resolve this question, the reaction between **56** and *m*-CPBA was performed in the presence of H₂¹⁸O (435 equiv.). By ESI-MS, ~30% ¹⁸O incorporation

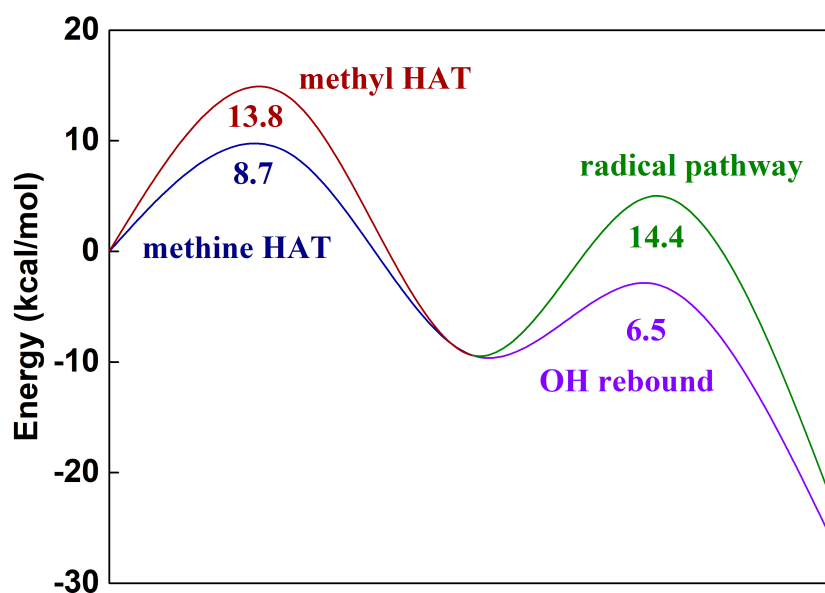


Figure 5.7. Energy profile for the formation of benzo-1,3-oxazine **58** (kcal/mol, S12g/TZ2P//BP86-D3/TDZP, including COSMO solvation and ZORA relativistic effects self-consistently).

was observed in the benzoxazine product **58** (fig. 5.8). This is a strong indication that the benzoxazine is formed through mechanism A, via the intermediate benzylic alcohol product, derived from hydroxylation by a putative $\text{Ni}^{\text{III}}\text{--O}^\bullet$ species, because such a species is likely to exchange with H_2^{18}O ,^{21,22} whereas the carboxamidate oxygen is unlikely to undergo exchange with H_2^{18}O .

This was supported by DFT analysis, which showed that although in the $\text{Ni}^{\text{III}}\text{--O}^\bullet$ species the benzyl hydrogen was further away from the oxygen atom (2.95 Å) than the methyl hydrogens (2.51 Å), the barrier for HAT was found to be significantly lower for the benzylic (7.1 kcal/mol) than the methyl (11.8 kcal/mol) hydrogen atoms (fig. 5.7). For the subsequent step (sch. 5.2), where either hydroxide radical rebound (mechanism A) or carboxamide O-atom radical coupling (mechanism B), DFT also supports the experimental observations. The barrier for the rebound pathway was found to be substantially lower (7.4 vs. 12.5 kcal/mol, fig. 5.7), corroborating the results from the isotopic labelling experiments. This allowed to conclude that a metal-based oxidant, distinct from the Ni^{III} -containing **57b**, is transiently formed when **56** was reacted with *m*-CPBA, and causes the oxidation of the supporting ligand.

The formation of degradation product **58** demonstrates that the putative $\text{Ni}^{\text{III}}\text{--O}^\bullet$ intermediate can be reduced by the transfer of one of the ligand's hydrogen atoms. In the reaction

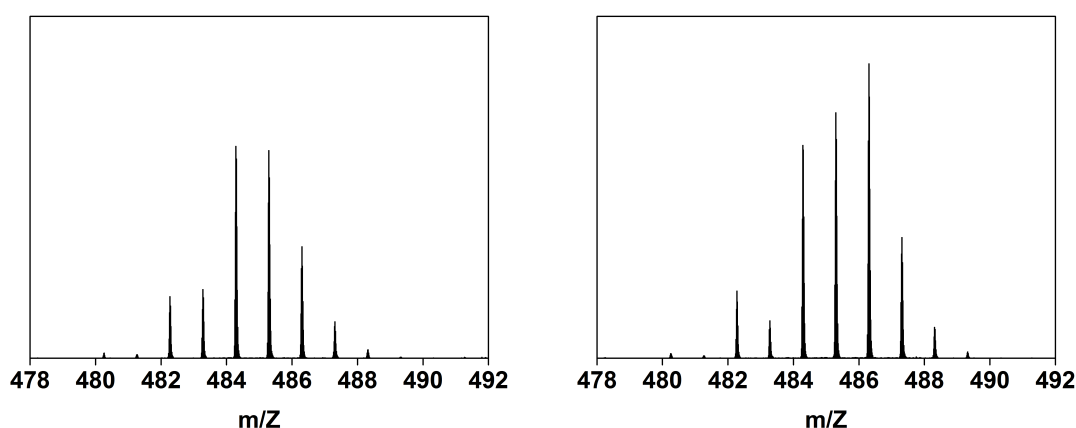
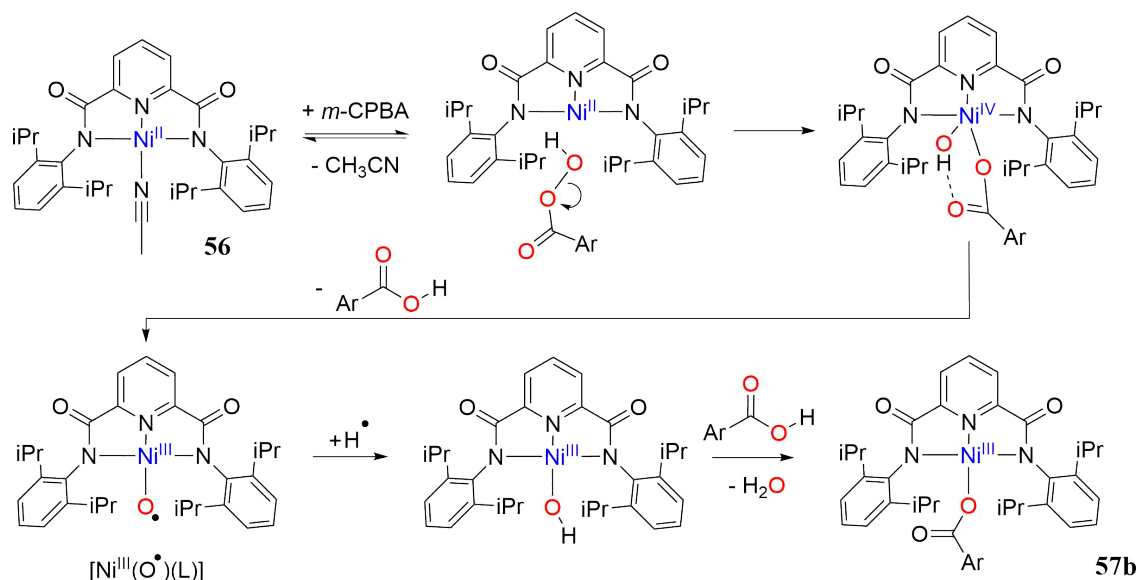


Figure 5.8. ESI-MS of the post-decay mixtures of (**56** + *m*-CPBA) in the presence of excess H₂O (natural abundance, left) and H₂¹⁸O (right).

between **56** and *m*-CPBA, one can postulate that the observed species **57b** is formed by a similar process, in which an exogenous reductant, most likely the solvent, causes the conversion of Ni^{III}–O[•] to Ni^{III}–OH (sch. 5.3). The latter subsequently reacts with *m*-CBA via ligand exchange, to form **57b**. While the structure of the second EPR-active product (axial signal, fig. 5.3) in the reaction of **56** and *m*-CPBA cannot be confirmed, one possibility is that it is a Ni^{III} species supported by the oxidised ligand (thus a Ni^{III} ion supported by **58**).



Scheme 5.3. Hypothetical mechanism for the formation of **57b** from the oxidation of **56** with *m*-CPBA.

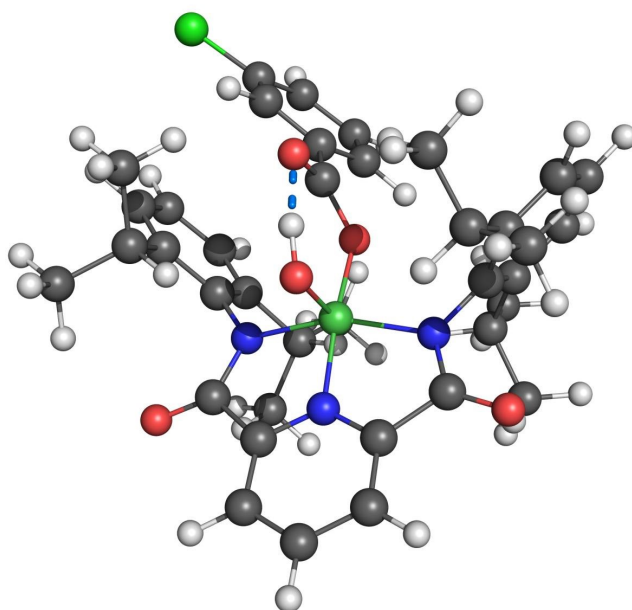


Figure 5.9. DFT-optimised structure obtained after binding of *m*-CPBA to **56**, in which the HO–OCOAr is broken spontaneously. The proton of the hydroxyl is involved in an intramolecular H-bond towards the *m*-CBA, which after proton transfer leads to the *m*-CBA and the Ni^{III}–oxyl species (obtained at BP86-D3/TDZP, including COSMO solvation and ZORA relativistic effects self-consistently).

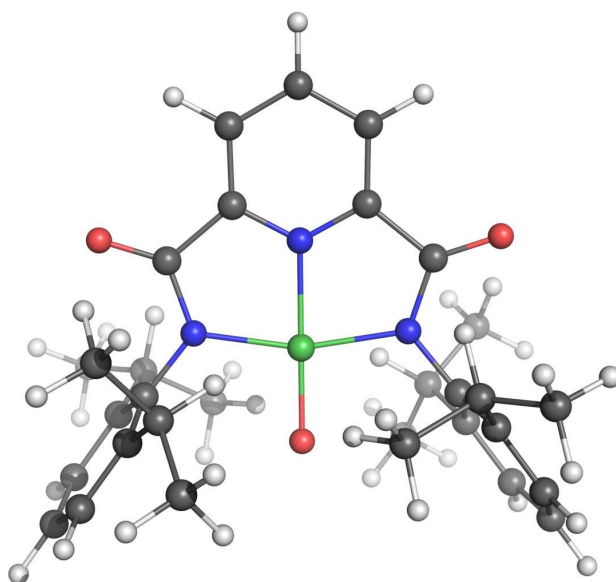


Figure 5.10. DFT-optimised Structure of the Ni^{III}–oxyl species (obtained at BP86-D3/TDZP, including COSMO solvation and ZORA relativistic effects self-consistently).

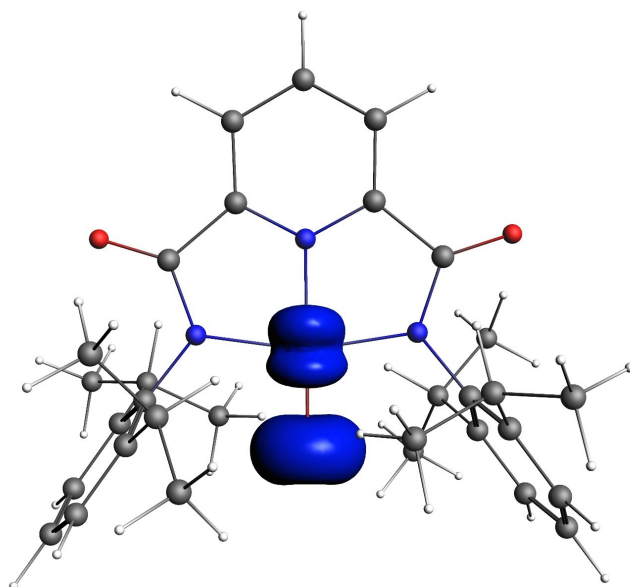


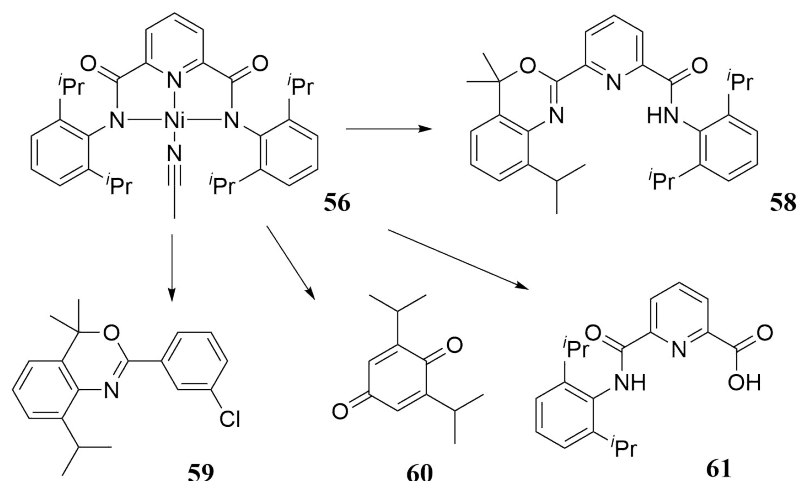
Figure 5.11. Spin-density of the Ni^{III} -oxyl species (obtained at S12g/TZ2P//BP86-D3/TDZP, including COSMO solvation and ZORA relativistic effects self-consistently). The MDC-m spin-density charges indicate a total spin of 1.04 on the oxygen, 0.86 on the nickel, 0.04 on the nitrogens, with the remaining spin density scattered over the ligand.

5.4.2 Secondary ligand degradation products

Other minor products were identified from the decay of the (**56** + *m*-CPBA) reaction mixture (sch. 5.4), which were characterised by NMR and mass spectrometry. The benzoxazine **59** was obtained in trace amounts ($\sim 1\%$ based on starting $\text{H}_2\text{pyN}_2^{\text{iPr}_2}$ amount), and results from the condensation of hydroxylated 2,6-diisopropylaniline and 3-chlorobenzoic acid. 2,6-Diisopropylquinone (**60**) was isolated in 6% yield, and is likely derived from the 2,6-diisopropylphenylaniline moiety of the ligand. The complementary fragment of the ligand, 6-((2,6-diisopropylphenyl)carbamoyl)picolinic acid (**61**) was observed by GC-MS ($m/Z = -325.1558$, $[\text{M} - \text{H}]^-$) but could not be isolated.

5.5 Oxidation of exogenous substrates

It was demonstrated in chapter 3 that $[\text{Ni}^{\text{III}}(\text{OX})(\text{pyN}_2^{\text{Me}_2})]$ complexes were not capable of oxidising cyclohexane ($\text{BDE}_{\text{C-H}} = 99 \text{ kcal/mol}$).^{23,24} The putative $\text{Ni}^{\text{III}}-\text{O}^\bullet$ is likely to be a more potent oxidant than the $[\text{Ni}^{\text{III}}(\text{OX})(\text{pyN}_2^{\text{Me}_2})]$ complexes. Previous experimental and computational studies have predicted $\text{Ni}^{\text{IV}}=\text{O}/\text{Ni}^{\text{III}}-\text{O}^\bullet$ entities to be powerful oxidants.^{7,25,26} **56** and *m*-CPBA were reacted in the presence of excess cyclohexane



Scheme 5.4. Ligand degradation products identified from the post-decay mixture of **56** + *m*-CPBA.

(80% by volume). Cyclohexanol, the hydroxylated product of cyclohexane, was found in trace amounts by GC-MS. The putative transient $\text{Ni}^{\text{III}}\text{--O}^\bullet$ is thus capable of oxidising non-activated, alkylic C-H bonds, and is a superior oxidant compared to well-characterised $[\text{Ni}^{\text{III}}(\text{OX})(\text{pyN}_2^{\text{Me}_2})]$ complexes.

5.6 Conclusions

In conclusion, the reaction of **56** with *m*-CPBA led to the formation of a stable Ni^{III} species, $[\text{Ni}^{\text{III}}(\text{pyN}_2^{\text{iPr}_2})(\text{OCOC}_6\text{H}_4\text{Cl})]$. The analysis of organic decay products led to surmise the existence of a more powerful, transient $\text{Ni}^{\text{III}}\text{--O}^\bullet$ precursor to this stable Ni^{III} species. The slow reaction of *m*-CPBA and instability of the $\text{Ni}^{\text{III}}\text{--O}^\bullet$ prevented its spectroscopic observation. When compared to the previously investigated $[\text{Ni}^{\text{III}}(\text{OX})(\text{pyN}_2^{\text{Me}_2})]$ this formally Ni^{IV} moiety demonstrated a greater oxidative power, reacting with strong C-H bonds in cyclohexane and effecting the degradation of the supporting ligand. The $\text{Ni}^{\text{III}}\text{--O}^\bullet$ mediated ligand oxidation resulted in the unexpected formation of benzoxazine **58**. Future efforts will focus on the stabilisation of the $\text{Ni}^{\text{III}}\text{--O}^\bullet$ to facilitate its isolation.

5.7 Experimental section

Physical Methods

Electronic absorption spectra were recorded on a Hewlett Packard (Agilent) 8453 diode array spectrophotometer (190-1100 nm range) in quartz cuvettes cooled using a liquid nitrogen cooled cryostat from Unisoku Scientific Instruments (Osaka, Japan). ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR analyses were performed on an Agilent MR400 instrument (400.13 MHz for ^1H NMR and 100.61 MHz for $^{13}\text{C}\{^1\text{H}\}$ NMR). GC-MS was performed using a GCT Premier Micromass time of flight mass spectrometer. Electrospray ionization (ESI) mass spectra were acquired using a Micromass time of flight spectrometer (TOF), interfaced to a Waters 2690 HPLC, or by direct injection in the mass spectrometry instrument. ATR-FTIR spectra were recorded on a Perkin-Elmer Spectrum 100 Fourier transform infrared spectrometer. Electron paramagnetic resonance spectra were recorded on a Bruker EMX spectrometer, equipped with an Oxford Instruments CE 5396, ESR9 continuous flow cryostat and an Oxford Instruments CE 5396 precision temperature controller, using liquid nitrogen cooling.

Materials and synthesis

Reactions with air-sensitive materials were conducted under an inert atmosphere using standard Schlenk techniques or in a nitrogen atmosphere glove-box. All solvents and reagents were purchased from commercial sources and used as received, unless otherwise stated. Anhydrous CH_3CN and CH_2Cl_2 were obtained by distillation over CaH_2 , and anhydrous acetone was obtained by distillation over B_2O_3 . *m*-CPBA was purified by dissolving in CH_2Cl_2 and washing with a pH 7.4 KH_2PO_4 buffer. Purity of the *m*-CPBA product (>95%) was confirmed by ^1H NMR. *N,N'*-(2,6-diisopropylphenyl)pyridine-2,6-dicarboxamide was prepared according to a reported procedure.²⁷

Synthesis of $[\text{Ni}^{\text{II}}(\text{CH}_3\text{CN})(\text{pyN}_2^{\text{iPr}_2})]$, acetonitrile(*N,N'*-bis(2,6-diisopropylphenyl)-2,6-pyridinedicarboxamido)nickel(II), **56**

The reaction was conducted under an inert nitrogen atmosphere. *N,N'*-(2,6-diisopropylphenyl)pyridine-2,6-dicarboxamide ($\text{H}_2\text{pyN}_2^{\text{iPr}_2}$, 0.350 g, 0.72 mmol) was dissolved in anhydrous THF (6 ml). Addition of NaH (60% dispersion in mineral oil, 0.058 g, 1.4 mmol, 2 eq.) resulted in immediate gas evolution and caused the solution to turn pale yellow. When bubbling ceased, $\text{Ni}(\text{OTf})_2$ (0.258 mg, 0.72 mmol, 1 eq.) was added, followed by

1 mL of anhydrous CH₃CN. A red solution, with a small amount of precipitate, formed; after stirring for 1 h at room temperature, the solvent was removed *in vacuo*. The resulting solids were taken up in anhydrous CH₂Cl₂ (20 ml), filtered, and evaporated to yield the product as a red-brown powder (0.268 mg, 0.46mmol, 64%). Crystals suitable for X-ray diffraction were obtained by diffusion of Et₂O into a concentrated CH₂Cl₂ solution.

δ H (400 MHz, CDCl₃): 8.08 (1H, t, J = 7.7 Hz, 4-py), 7.79 (2H, d, J = 7.7 Hz, 3,5-py), 7.10-7.06 (2H, m, ArH), 7.05-7.00 (4H, m, ArH), 3.80 (4H, hept., CH(CH₃)₂, J = 6.9 Hz), 1.40 (12H, d, CH(CH₃)₂, J = 6.9 Hz), 1.40 (12H, d, CH(CH₃)₂, J = 6.9 Hz), 1.25 (3H, s, CH₃CN).

δ C (101 MHz, CDCl₃): 166.9 (NC=O), 151.1 (pyridine CH), 144.3 (aniline Cq), 141.5 (pyridine Cq), 141.2 (aniline Cq), 125.8 (aniline CH), 123.6 (pyridine CH), 122.7 (aniline CH), 122.6 (CH₃CN), 28.9 (CH(CH₃)₂), 24.3 (CH(CH₃)₂), 23.6 (CH(CH₃)₂), 0.7 (CH₃CN).

ESI-MS (m/z): Found: 583.2583 ([M + H]⁺, C₃₃H₄₁N₄NiO₂ requires 583.2578).

ν_{max} (ATR-FTIR) /cm⁻¹: 2961 (CH), 2926 (CH), 2866 (CH), 2323w (C $\equiv$ N), 2296w, 1633s (C=O), 1605 (C=O), 1462, 1441, 1370, 1360, 800m, 770s, 747, 737, 680m.

λ_{max} (THF) /nm: 430 (ϵ /M⁻¹ cm⁻¹ 1000), 550 sh (130).

Synthesis of [Ni^{II}(OCOC₆H₄Cl)(pyN₂^{iPr₂})]Et₄N, tetraethylammonium (3-chlorobenzoato)(*N,N'*-bis(2,6-diisopropylphenyl)-2,6-pyridinedicarboxamido)nickelate(II), 57a

A crude tetraethylammonium 3-chlorobenzoate material was prepared by metathesis of Et₄NCl.H₂O (101 mg, 0.55mmol) and sodium 3-chlorobenzoate (100 mg, 0.55mmol; obtained from equimolar amounts of NaOH and 3-chlorobenzoic acid), by dissolving both in CH₃OH (5 mL), removing the solvent *in vacuo*, and taking up the residue in CH₃CN (10 mL). A white solid (presumably NaCl) was filtered off, and the oily product obtained after evaporation of CH₃CN. The crude Et₄N(OCOC₆H₄Cl) was added to **56** (0.314 g, 0.54 mmol), dissolved in CH₃CN (3 ml), causing the solution to immediately turn from brown-red to bright red. After 5 minutes stirring, Et₂O (20 ml) was layered on top of the solution. Over the course of 5 days, crystals of the product formed, and were recovered by decanting the solution (0.330 g, 0.40mmol, 74%). Crystals suitable for X-ray diffraction were identified in the product.

δ H (400 MHz, CDCl₃): 7.85 (1H, t, J = 7.7 Hz, 4-py), 7.51 (2H, d, J = 7.7 Hz, 3,5-py), 6.90 (1H, d, J = 7.2 Hz, C₆H₄ClCO₂), 6.87–6.70 (7H, m, ArH), 6.59 (1H, d, J = 7.4 Hz), 6.53 (1H, s, C₆H₄ClCO₂), 4.28 (4H, hept., J = 6.5 Hz, CH(CH₃)₂), 2.83–2.72 (8H, m,

NCH_2CH_3), 1.33 (12H, d, $J = 6.5$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.13 (12H, d, $J = 6.5$ Hz, $\text{CH}(\text{CH}_3)_2$), 0.95 (12H, br, NCH_2CH_3).

δC (101 MHz, CDCl_3): 169.6 ($\text{C}_6\text{H}_4\text{ClC=O}$), 166.9 (NC=O), 152.3 (2,6-py), 145.0 (Cq Ar.), 141.9 (Cq Ar.), 139.6 (Cq Ar.), 138.4 (4-py), 131.8 (Cq Ar.), 128.0 (CH Ar.), 127.7 (CH Ar.), 127.4 (CH Ar.), 125.9 (CH Ar.), 124.0 (CH Ar.), 121.9 (CH Ar.), 121.8 (3,5-py), 52.1 (NCH_2CH_3), 28.9 ($\text{CH}(\text{CH}_3)_2$), 25.3 ($\text{CH}(\text{CH}_3)_2$), 23.5 ($\text{CH}(\text{CH}_3)_2$), 7.3 (NCH_2CH_3).

ESI-MS (m/Z): Found: 696.2130 ($[\text{Ni}(\text{ArCO}_2)(\text{pyN}_2^{\text{iPr}_2})]^-$, $\text{C}_{38}\text{H}_{41}\text{ClN}_3\text{NiO}_4$ requires 696.2139).

ν_{max} (ATR-FTIR) $/\text{cm}^{-1}$: 3058 (CH) 2956 (CH), 2865 (CH), 1605s (C=O), 1584, 1566, 1440, 1372, 1348s, 1002, 836, 757, 744s, 682m.

λ_{max} (acetone) $/\text{nm}$ 380 ($\epsilon / \text{M}^{-1} \text{cm}^{-1}$ 4000), 470 sh (700).

Reaction of **56** with *m*-CPBA

The reaction was monitored by electronic absorption spectroscopy. 2 ml of a 0.5 mM acetone (or CH_3CN) solution of **56** were placed in a cuvette at 25 °C. 8 μL of a 0.25 M solution of *m*-CPBA in acetone were added under stirring. New absorption features with $\lambda_{\text{max}} = 560$ nm and a shoulder at 760 nm, slowly appeared, reaching the maximum intensity after 350 s.

Reaction of **57a** with magic blue

2 ml of a 0.5 mM acetone solution of **57a** were cooled to -80 °C in a cuvette. 66 μL of a freshly prepared 15 mM solution of tris(4-bromophenyl)ammoniumyl hexachloroantimonate (magic blue) in CH_3CN were added under continuous stirring. Immediately, bands attributed to the oxidised product (580 nm, shoulder at 760 nm) appeared.

The reaction was repeated on a larger scale for the analysis of decay products. **57a** (24 mg, 0.03mmol) was dissolved in 20 mL of acetone in a Schlenk flask immersed in a CH_3CN /liquid nitrogen bath (-45 °C). Magic blue (23 mg, 1 eq.) was added under stirring, causing a change in colour from red to purple; after 10 minutes the mixture was allowed to warm up to room temperature. The acetone was evaporated, the residues taken up in CH_2Cl_2 and washed with 1 M HCl. ^1H NMR, ESI-MS, GC-MS and TLC analyses showed no formation of ligand decay (oxidised) products.

EPR of the Ni^{III} intermediates

The EPR spectra of the Ni^{III} intermediates were recorded on a frozen solution in an EPR tube, prepared according to the above procedure. The EPR spectrum was recorded at 77 K, 9.2 GHz, 2 mW microwave power, with a 100 mT field sweep in 83 s, and 0.5 mT, 100 kHz field modulation. Integration, simulation, and fitting were executed with Matlab and the easySpin computational package.²⁸ Spin quantification was effected by double integration of the signals and comparison with a standard radical sample (TEMPO, 0.5 mM). The signals were fitted as $S = \frac{1}{2}$ electron spin systems, with anisotropic g tensors and inhomogeneous line broadening. The spectrum of the product of the reaction of **57a** + magic blue was simulated as a single species with $g_x = 2.42$, $g_y = 2.26$, $g_z = 1.99$. The spectrum of the reaction mixture from **56** + *m*-CPBA was simulated as a mixture of the same species, plus a second species ($g_{\perp} = 2.23$, $g_{\parallel} = 2.01$) in nearly equal amounts (55:45%).

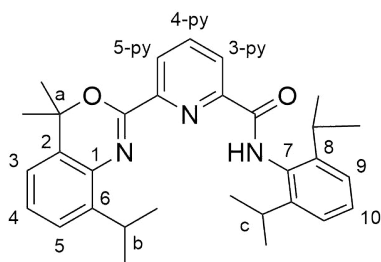
Mass spectrometry of the Ni^{III} species

ESI-MS analysis of the Ni^{III} species was conducted on solutions prepared according to the above procedures (**56** + *m*-CPBA and **57a** + magic blue), transferred to a glass vial and diluted by 50% by the addition of cold (~ -40 °C) CH₃CN. These solutions were frozen in liquid nitrogen, and directly injected in the mass spectrometer immediately after thawing.

Analysis of the decay products of the reaction of **56** + *m*-CPBA

The above reaction was scaled up for the structural characterization of the decay products. 227 mg of **56** (0.39 mmol) was dissolved in 100 ml of acetone in a round bottom flask and cooled in an ice-water bath. Solid *m*-CPBA (135 mg, 2 eq.) was added under stirring, causing the purple-black colour to develop over the course of a few minutes. After 1 hour, the solution was allowed to warm to room temperature and left to decay for a further 12 hours. The solvent was evaporated, the solids redissolved in CH₂Cl₂ and washed with 1 M HCl. The mixture was analysed by ESI-MS, GC-MS, and ¹H NMR. The compounds were isolated by column chromatographic separation on silica (eluent: hexanes/ethyl acetate 10/1). *m*-chlorobenzoic acid was not quantitatively recovered because of long elution time and strong interaction with the silica. Its amount was estimated by ¹H NMR integration of the crude acidified product, using dimethylformamide as an internal standard, as >90%, based on the original *m*-CPBA amount added to the reaction mixture. The benzoxazine **59** (sch. 5.4), 2,6-diisopropylbenzoquinone (**60**) were also obtained from the separation and identified through NMR and mass spectrometry.

***N*-(2,6-diisopropylphenyl)-6-(8-isopropyl-4,4-dimethyl-4H-benzo[d][1,3]oxazin-2-yl)picolinamide, 58**



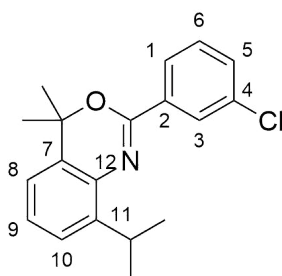
58 was isolated in 35% yield. Crystals suitable for diffraction were obtained by addition of H₂O to an ethanolic solution of **58** in an NMR tube.

δ H (400 MHz, CDCl₃): 9.74 (1H, s, NH), 8.49 (1H, d, J = 7.8 Hz, 6-py), 8.38 (1H, d, J = 7.8 Hz, 2-py), 8.01 (1H, t, J = 7.8 Hz, 4-py), 7.46–7.30 (1H, m, CH¹⁰), 7.28–7.23 (3H, m, overlaps with residual CHCl₃, CH^{5,9}), 7.21 (1H, t, J = 7.5 Hz, CH⁴), 7.01 (1H, d, J = 7.5 Hz, CH³), 3.95 (1H, hept., J = 7.0 Hz, CH^b), 3.19 (2H, hept, J = 6.9 Hz, CH^c), 1.72 (6H, s, CH₃^a), 1.30 (6H, d, J = 7.0 Hz, CH₃^b), 1.26 (12H, d, J = 6.9 Hz, CH₃^c).

δ C (101 MHz, CDCl₃): 163.1 (C=O), 153.7 (C=N), 150.2 (6-py), 149.4 (2-py), 146.1 (C⁸), 144.1 (C⁶), 138.0 (4-py), 135.0 (C¹), 131.4 (C²), 131.4 (C⁷), 128.1 (C¹⁰), 127.3 (C⁴), 126.2 (6-py), 125.3 (C⁵), 123.7 (2-py), 123.6 (C⁹), 119.8 (C³), 78.9 (C^a), 29.1 (CH^c), 28.6 (CH^a), 27.4 (CH^b), 23.6 (CH₃^c), 23.39 (CH₃^b).

ESI-MS (m/z): Found: 484.2968 ([M + H]⁺, C₃₁H₃₈N₃O₂ requires 484.2964).

2-(3-chlorophenyl)-8-isopropyl-4,4-dimethyl-4H-benzo[d][1,3]oxazine, 59



59 was obtained in trace amounts (~1%).

δ H (400 MHz, CDCl₃): 8.12 (1H, br, CH₃), 8.07 (1H, d, J = 7.8 Hz, CH¹), 7.45 (1H, br, d, J = 7.8 Hz, CH⁵), 7.38 (1H, t, J = 7.8 Hz, CH⁶), 7.25 (1H, d, J = 7.6 Hz, overlaps with residual CHCl₃, CH¹⁰), 7.17 (1H, t, J = 7.6 Hz, CH⁹), 7.00 (1H, d, J = 7.6 Hz, CH⁸),

3.94 (1H, hept., $J = 7.0$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.69 (6H, s, $\text{OC}(\text{CH}_3)_2$), 1.30 (6H, d, $J = 7.0$ Hz, $\text{CH}(\text{CH}_3)_2$).

δC (101 MHz, CDCl_3): 154.0 ($\text{C}=\text{N}$), 143.8 (C^{11}), 135.5 ($\text{C}^{2/4}$), 135.2 (C^{12}), 134.2 ($\text{C}^{4/2}$), 131.2 (C^7), 130.9 (C^1), 129.4 (C^6), 127.8 (C^3), 126.6 (C^9), 126.0 (C^5), 125.13 (C^{10}), 119.6 (C^8), 78.5 ($\text{OC}(\text{CH}_3)_2$), 28.3 ($\text{OC}(\text{CH}_3)_2$), 27.2 ($\text{CH}(\text{CH}_3)_2$), 23.4 ($\text{CH}(\text{CH}_3)_2$).

ESI-MS (m/z): Found: 314.1304 ($[\text{M} + \text{H}]^+$, $\text{C}_{19}\text{H}_{21}\text{ClNO}$ requires 314.1306).

2,6-Diisopropylbenzoquinone, **60**

was isolated in 6% yield. Spectra correspond to previous literature reports.²⁹

δH (400 MHz, CDCl_3): 6.47 (1H, s), 3.07 (2H, hept., $J = 6.9$ Hz), 1.13 (12H, d, $J = 6.9$ Hz).

Reaction of **56** with *m*-CPBA – isotopic labelling with H_2^{18}O

The reactions were conducted in Schlenk flasks under inert atmosphere; a blank reaction was conducted in parallel using the same nickel complex and *m*-CPBA stock solutions, and natural abundance (non-enriched) H_2O . To a stirred solution of **56** in anhydrous CH_3CN (3 mL, 1.7 mM), 40 μL of H_2^{18}O (97 atom% enrichment) were added, followed by 2 equivalents of *m*-CPBA. The oxidised intermediate was allowed to form and decay, and after 12 hours the solvent was removed, followed by addition of CH_2Cl_2 and washing with 1 M HCl. The isotopic content of the products was analysed by ESI-MS. A complicating factor was that $[\text{O}^{18}]\textbf{58}$ has the same nominal mass as unmodified $\text{H}_2\text{pyN}_2^{i\text{Pr}_2}$. Nevertheless, the corresponding peak was 50% more intense in the experiment with H_2^{18}O , as opposed to a blank with natural abundance water, after normalising the peak corresponding to **58** (fig. 5.8). The extent of ^{18}O incorporation in the product was evaluated as $\sim 30\%$, after subtracting the peak intensity due to $\text{H}_2\text{pyN}_2^{i\text{Pr}_2}$.

Reaction of *N,N'*-(2,6-diisopropylphenyl)pyridine-2,6-dicarboxamide with *m*-CPBA

N,N'-(2,6-diisopropylphenyl)pyridine-2,6-dicarboxamide (200 mg, 0.41 mmol) was dissolved in 40 mL of acetone and solid *m*-CPBA (156 mg, 0.91 mmol, 2.2 eq.) added to it under stirring. After 24 h an NaI test indicated the presence of unreacted oxidant; this was carefully quenched with aqueous $\text{Na}_2\text{S}_2\text{O}_3$. The crude mixture was analysed by ^1H NMR, ESI-MS, GC-MS and TLC, where no products other than the unmodified ligand $\text{H}_2\text{pyN}_2^{i\text{Pr}_2}$ were identified.

Oxidation of cyclohexane

56 (5 mg, 8.6 μmol) was dissolved in 1 mL of $[\text{D}_6]$ acetone; 4 mL of cyclohexane were added to the solution, followed by *m*-CPBA (3 mg, 17 μmol , 2 eq.). The mixture was allowed to react and decay under stirring for 12 hours; afterwards it was filtered on a cotton plug and analysed by GC-MS.

X-Ray diffraction methods

Single crystal X-ray data were collected at 100(2) K on a Bruker Apex II CCD diffractometer using graphite-monochromated Mo- $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$), an Oxford Cryo-systems Cobra low temperature device and a MiTeGen micromount. Bruker APEX³⁰ software was used to correct for Lorentz and polarization effects. The structures were solved and refined using the Bruker SHELXTL Software Package.^{31,32}

X-ray structure refinement notes

The crystal cell of **56** contains two independent, but isostructural, molecules in the asymmetric unit, and one disordered molecule of diethyl ether. The disorder was modelled with restraints applied to maintain geometry and displacement. The structure of **57a** contains one molecule of CH_3CN in the asymmetric unit. The structure of **58** contains a molecule of ethanol hydrogen-bonded to the N and N-H groups of **58**. The isopropyl groups are disordered and modelled with restraints and constraints (DFIX, SADI and EADP). The EtOH molecule is also disordered and was modelled and was modelled with restraints and constraints (SADI and EADP).

Table 5.1. Crystal data and structure refinement parameters for **56**, **57a**, and **58**.

	56	57a	58
Empirical formula	C ₇₀ H ₉₀ N ₈ Ni ₂ O ₅	C ₃₁ H ₆₄ ClN ₅ NiO ₄	C ₃₃ H ₄₃ N ₃ O ₃
Formula weight	1240.92	869.40	529.70
Temperature	100(2) K	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å	1.54178 Å
Crystal system	Monoclinic	Triclinic	Hexagonal
Space group	P 1 2 ₁ /c 1	P $\bar{1}$	P6 ₅
Unit cell dimensions	$a = 20.7514(7)$ Å $\alpha = 90^\circ$ $b = 21.5643(8)$ Å $\beta = 110.8990(10)^\circ$ $c = 16.1479(6)$ Å $\gamma = 90^\circ$	$a = 11.2143(4)$ Å $\alpha = 110.6620(10)^\circ$ $b = 13.9431(5)$ Å $\beta = 91.4110(10)^\circ$ $c = 16.1500(6)$ Å $\gamma = 106.7540(10)^\circ$	$a = 8.7435(4)$ Å $\alpha = 90^\circ$ $b = 8.7435(4)$ Å $\beta = 90^\circ$ $c = 69.045(3)$ Å $\gamma = 120^\circ$
Volume	3258.95(19) Å ³	2239.91(14) Å ³	2276.8(3) Å ³
Z	4	2	6
Density (calculated)	1.221 Mg/m ³	1.289 Mg/m ³	1.155 Mg/m ³
Absorption coefficient	0.612 mm ⁻¹	0.542 mm ⁻¹	0.581 mm ⁻¹
F(000)	2648	928	1716
Crystal size	0.050 x 0.150 x 0.180 mm ³	0.260 x 0.230 x 0.110 mm ³	0.21 x 0.19 x 0.04 mm ³
Theta range for data collection	1.41 to 27.51°	2.298 to 30.633°	3.841 to 68.386°
Index ranges	$-26 \leq h \leq 26$, $-14 \leq k \leq 14$, $-20 \leq l \leq 20$	$-16 \leq h \leq 16$, $-19 \leq k \leq 19$, $-23 \leq l \leq 23$	$-10 \leq h \leq 10$, $-10 \leq k \leq 10$, $-82 \leq l \leq 82$
Reflections collected	72448	49339	26441
Independent reflections	15480 [R(int) = 0.0443]	13768 [R(int) = 0.0318]	5575 [R(int) = 0.0588]
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.9701 and 0.8979	0.7461 and 0.6825	0.7531 and 0.5659
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	15480 / 16 / 795	13768 / 0 / 545	5575 / 8 / 384
Goodness-of-fit on F ²	1.020	1.025	1.031
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0402, wR2 = 0.0917	R1 = 0.0370, wR2 = 0.0881	R1 = 0.0577, wR2 = 0.1461
R indices (all data)	R1 = 0.0658, wR2 = 0.1019	R1 = 0.0505, wR2 = 0.0954	R1 = 0.0653, wR2 = 0.1516
Largest diff. peak and hole	0.750 and -0.720 e Å ⁻³	0.551 and -0.518 e Å ⁻³	0.256 and -0.227 e Å ⁻³

DFT methods

All calculations have been performed using the Amsterdam Density Functional (ADF)^{33,34} and QUILD³⁵ programs. Molecular orbitals were expanded in an uncontracted set of Slater type orbitals (STOs) of triple- ζ quality with double polarization functions (TZ2P), or the TDZP basis set which consists of triple- ζ quality on the metal and double- ζ quality on all other atoms, in both cases including one polarization function.^{36,37} Core electrons were not treated explicitly during the geometry optimizations (frozen core approximation³⁴). An auxiliary set of *s*, *p*, *d*, *f*, and *g* STOs was used to fit the molecular density and to represent the Coulomb and exchange potentials accurately for each SCF cycle. Geometries of all possible spin states were optimized with the QUILD³⁵ program using adapted delocalized coordinates until the maximum gradient component was less than 10^{-4} a.u.. Energies, gradients and Hessians (for vibrational frequencies) were calculated using BP86-D3,^{38–40} in all cases by including solvation effects through the COSMO¹² dielectric continuum model with appropriate parameters for the solvents.¹⁴ For computing Gibbs free energies, all small frequencies were raised to 100 cm^{-1} in order to compensate for the breakdown of the harmonic oscillator model.^{41,42} Scalar relativistic corrections have been included self-consistently in all calculations by using the zeroth-order regular approximation (ZORA).¹⁵ The geometry optimizations at the BP86-D3 level were performed with the TDZP basis set. Subsequent single-point calculations (with the TZ2P basis set) have been performed with S12g,¹¹ and all Time-Dependent DFT calculations were carried out with the SAOP potential⁴³ and the all-electron TZ2P basis set. For all calculations carried out with BP86-D3 the Becke⁴⁴ grid of Normal quality was used; calculations performed with SAOP with a Becke grid of Good quality, and S12g calculations were performed with a Becke grid of VeryGood quality.

References

- (1) Koola, J. D.; Kochi, J. K. *Inorg. Chem.* **1987**, *26*, 908–916.
- (2) Nagataki, T.; Tachi, Y.; Itoh, S. *Chem. Commun.* **2006**, *14*, 4016–4018.
- (3) Nagataki, T.; Ishii, K.; Tachi, Y.; Itoh, S. *Dalton Trans.* **2007**, *21*, 1120–1128.
- (4) Nagataki, T.; Itoh, S. *Chem. Lett.* **2007**, *36*, 748–749.
- (5) Balamurugan, M.; Mayilmurugan, R.; Suresh, E.; Palaniandavar, M. *Dalton Trans.* **2011**, *40*, 9413–9424.
- (6) Sankaralingam, M.; Vadivelu, P.; Suresh, E.; Palaniandavar, M. *Inorg. Chim. Acta* **2013**, *407*, 98–107.
- (7) Sankaralingam, M.; Balamurugan, M.; Palaniandavar, M.; Vadivelu, P.; Suresh, C. H. *Chem. Eur. J.* **2014**, *20*, 11346–11361.
- (8) Tokumaru, K.; Simamura, O. *Bull. Chem. Soc. Jpn.* **1962**, *35*, 1678–1683.
- (9) Bravo, A.; Bjorsvik, H.-R.; Fontana, F.; Minisci, F.; Serri, A. *J. Org. Chem.* **1996**, *61*, 9409–9416.
- (10) Ray, K.; Lee, S. M.; Que, L. *Inorg. Chim. Acta* **2008**, *361*, 1066–1069.
- (11) Swart, M. *Chem. Phys. Lett.* **2013**, *580*, 166–171.
- (12) Klamt, A.; Schüürmann, G. *J. Chem. Soc., Perkin Trans. 2* **1993**, 799–805.
- (13) Pye, C. C.; Ziegler, T. *Theor. Chem. Acc.* **1999**, *101*, 396–408.
- (14) Swart, M.; Räsler, E.; Bickelhaupt, F. M. *Eur. J. Inorg. Chem.* **2007**, *2007*, 3646–3654.
- (15) Van Lenthe, E.; Baerends, E.; Snijders, J. J. *Chem. Phys.* **1993**, *99*, 4597–4610.
- (16) Picot, A.; Lusinchi, X. *Tetrahedron Lett.* **1973**, *14*, 903–906.
- (17) Kul'nevich, V. G.; Gromachevskaya, E. V.; Kosulina, T. P. *Chem. Heterocycl. Compd.* **1984**, *20*, 776–778.
- (18) Kolotova, N. V.; Koz'minykh, V. O.; Dolbilkina, Ā. V.; Koz'minykh, E. N.; Kolla, V. Ā.; Shelenkova, S. A. *Pharm. Chem. J.* **1998**, *32*, 486–489.
- (19) Fischer, O.; Schmidt, C. *Ber. Dtsch. Chem. Ges.* **1884**, *17*, 1889–1895.
- (20) Baeyer, A.; Villiger, V. *Ber. Dtsch. Chem. Ges.* **1903**, *36*, 2774–2796.
- (21) Nam, W.; Valentine, J. S. *J. Am. Chem. Soc.* **1993**, *115*, 1772–1778.
- (22) Lee, K. A.; Nam, W. *J. Am. Chem. Soc.* **1997**, *119*, 1916–1922.
- (23) Tian, Z.; Fattahi, A.; Lis, L.; Kass, S. R. *J. Am. Chem. Soc.* **2006**, *128*, 17087–17092.
- (24) Luo, Y., *Handbook of Bond Dissociation Energies in Organic Compounds*; Taylor & Francis: 2002.
- (25) Pierpont, A. W.; Cundari, T. R. *Inorg. Chem.* **2010**, *49*, 2038–2046.
- (26) Corona, T.; Pfaff, F. F.; Acuña-Parés, F.; Draksharapu, A.; Whiteoak, C. J.; Martin-Diaconescu, V.; Lloret-Fillol, J.; Browne, W. R.; Ray, K.; Company, A. *Chem. Eur. J.* **2015**, *21*, 15029–15038.
- (27) Wasilke, J.; Wu, G.; Bu, X.; Kehr, G.; Erker, G. *Organometallics* **2005**, 4289–4297.
- (28) Stoll, S.; Schweiger, A. *J. Magn. Reson.* **2006**, *178*, 42–55.
- (29) Pramanik, C.; Kotharkar, S.; Patil, P.; Gotrane, D.; More, Y.; Borhade, A.; Chaugule, B.; Khaladkar, T.; Neelakandan, K.; Chaudhari, A.; Kulkarni, M. G.; Tripathy, N. K.; Gurjar, M. K. *Org. Process Res. Dev.* **2014**, *18*, 152–156.
- (30) Bruker APEX v2014.11-0, Bruker AXS Inc., Madison, Wisconsin, USA.
- (31) SHELXL-2014, Bruker AXS Inc., Madison, Wisconsin, USA.
- (32) Sheldrick, G. *Acta Crystallogr. Sect. A* **2008**, *64*, 112–122.
- (33) Baerends, E. J. et al. ADF2013.01.; SCM, Amsterdam, 2013.
- (34) Te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Fonseca Guerra, C.; van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931–967.
- (35) Swart, M.; Bickelhaupt, F. M. *J. Comput. Chem.* **2008**, *29*, 724–734.
- (36) Van Lenthe, E.; Baerends, E. J. *J. Comput. Chem.* **2003**, *24*, 1142–1156.
- (37) Chong, D. P.; van Lenthe, E.; van Gisbergen, S.; Baerends, E. J. *J. Comput. Chem.* **2004**, *25*, 1030–1036.
- (38) Becke, A. *Phys. Rev. A* **1988**, *38*, 3098–3100.
- (39) Perdew, J. *Phys. Rev. B* **1986**, *33*, 8822–8824. Erratum: *Ibid.* *34*, 7406.
- (40) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104.

- (41) Averkiev, B. B.; Truhlar, D. G. *Catal. Sci. Tech.* **2011**, *1*, 1526–1529.
- (42) Klein, J. E.; Dereli, B.; Que, L.; Cramer, C. J. *Chem. Commun.* **2016**, *52*, 10509–10512.
- (43) Schipper, P.; Gritsenko, O.; Van Gisbergen, S.; Baerends, E. *J. Chem. Phys.* **2000**, *112*, 1344–1352.
- (44) Franchini, M.; Philipsen, P. H. T.; Visscher, L. *J. Comput. Chem.* **2013**, *34*, 1819–1827.

Chapter 6

Synthesis of Cobalt(II) and Zinc(II) Pyridinedicarboxamidate Complexes

The XRD data collection and structure solutions and refinements described in this chapter were done by Dr Brendan Twamley (Trinity College Dublin).

6.1 Introduction

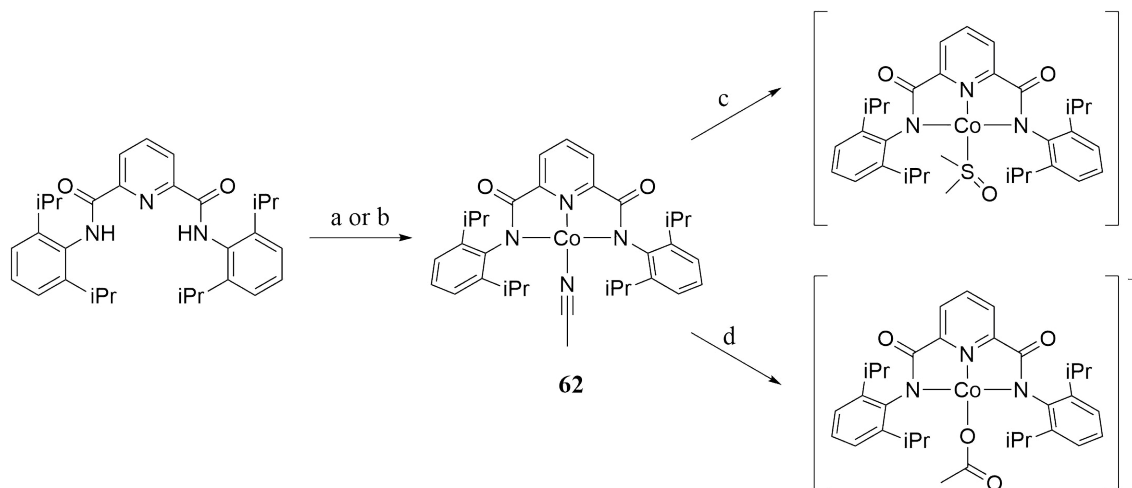
In the previous chapters it was have demonstrated that $\text{Ni}^{\text{III}}\text{--O--X}$ species, and in particular the $\text{Ni}^{\text{III}}\text{--OAc}$ complex **45b** (chapter 3), are viable oxidants, capable of activating C–H bonds. Their reactivity was suggestive of high-valent late-transition metal complexes possessing a high oxidising power, greater than analogous Fe or Mn species. In order to further explore the effect of the central metal, its d electron count and electronegativity, it was decided to expand the scope of investigation to other first transition metals.

The availability of a series of compounds with structures that are as close as possible is important to this end. Luckily, pyridinedicarboxamidate ligands have proven quite versatile in forming complexes with several mid- and late-transition metals. Ions with d^8 and d^9 electronic structure have given rise to the largest group of such compounds, and they possess similar tetracoordinate, square planar geometries, as a result of both the central metal's and the pincer ligand's preferences. Nickel(II) complexes have been extensively studied by Erker Holm,^{1–3} and there are also examples with heavier d^8 metals, such as palladium(II),^{2,4} and gold(III).⁵ Tolman has demonstrated the synthesis of several copper(II) complexes.^{6–8} Amongst the metal ions with lower d electron count, Ruthenium(II), ruthenium(IV),¹ Fe(III), Co(III)⁹ complexes of $\text{pyN}_2^{\text{R}_2}$ ligands have been reported, but they were 5- or 6- coordinate.

Nevertheless, with the appropriate choice of synthetic conditions and of the steric properties of the ligand, 4-coordinate species could be expected to be prepared even for mid-transition metals such as Fe and Co. I have preferred to focus on the $\text{pyN}_{2\text{iPr}_2}$ ligand variant, with isopropyl substituents, as its increased bulk is likely to contribute to better stability of the complexes in comparison to the methylated analogue used in chapters 2 to 4.

A second intriguing question is whether $\text{pyN}_2^{\text{R}_2}$ acts as an innocent supporting ligand, or can contribute to the redox behaviour of the systems:^{10,11} the presence of three aromatic rings, and in particular of the Ar–N groups, can in principle suggest it is capable of stabilising a radical cation, through delocalisation over an extended π system. The carboxamide groups, though, interrupt the complete conjugation of the three aromatic rings (*i.e.* the system is cross-conjugated), and presumably reduce the extent of this effect. To this goal, I have also explored the synthesis of zinc complexes, as the zinc(II) ion has similar properties in terms of size and Lewis acidity to its neighbours in the first transition series of the periodic table, but is commonly not redox active. This chapter will describe the synthesis of cobalt(II) and zinc(II) complexes, and initial studies on their chemical transformations, with the future goal of generating reactive M–OAc species from them.

6.2 Synthesis and characterisation of a cobalt(II) acetonitrile complex



Scheme 6.1. Synthesis of **62**, and putative products formed in the NMR scale reactions. a) BuLi (2.2 eq.), CoCl₂, THF, CH₃CN, recrystallised from CH₂Cl₂/Et₂O. b) KH (2.1 eq.), CoCl₂, CH₃CN. c) [D₆]DMSO. d) Bu₄NOAc (1.5 eq.).

A cobalt(II) complex [Co^{II}(CH₃CN)(pyN₂^{iPr₂})] (**62**) was obtained by metallation of the ligand pyN₂^{iPr₂} with CoCl₂, in the presence of a strong base (sch. 6.1). H₂pyN₂^{iPr₂}, dissolved in THF, was deprotonated with BuLi (2.2 eq.), and reacted with anhydrous CoCl₂ (1 eq.), forming a dark green solution. After removal of the THF, introduction of the CH₃CN ligand together with CH₂Cl₂ caused the solution to turn red. Filtration to remove insoluble byproducts, followed by addition of Et₂O, resulted in the formation of **62** as red-orange crystals (21% yield), together with a purple amorphous material. The crystalline product was manually separated and characterised by X-ray diffraction, ¹H NMR, ESI-MS, AT-FTIR and UV-Vis spectroscopies.

An alternative procedure, employing KH (2.1 eq.) in CH₃CN instead of BuLi, provided a greatly improved yield (86%). The product was confirmed as identical to the previous by NMR spectroscopy. Probably, the modest yield obtained in the first synthesis is to be attributed to a reduced driving force for the formation of solid LiCl, as opposed to KCl, leaving byproducts of the type Li_x[Co^{II}(Cl)_x(pyN₂^{iPr₂})].

The crystal structure of **62** revealed a four-coordinate, square planar complex, with geometry index¹² $\tau_4 = 0.11$. **62** was isostructural to the Ni^{II} analogue [Ni^{II}(CH₃CN)(pyN₂^{iPr₂})] (**56**, chapter 5), with almost identical structural parameters (table 6.1). This result was encouraging, as it proved that the pyN₂^{iPr₂} is capable of stabilising a square planar coordination geometry even for *d*⁷ ions, whose preference for this geometry is less marked

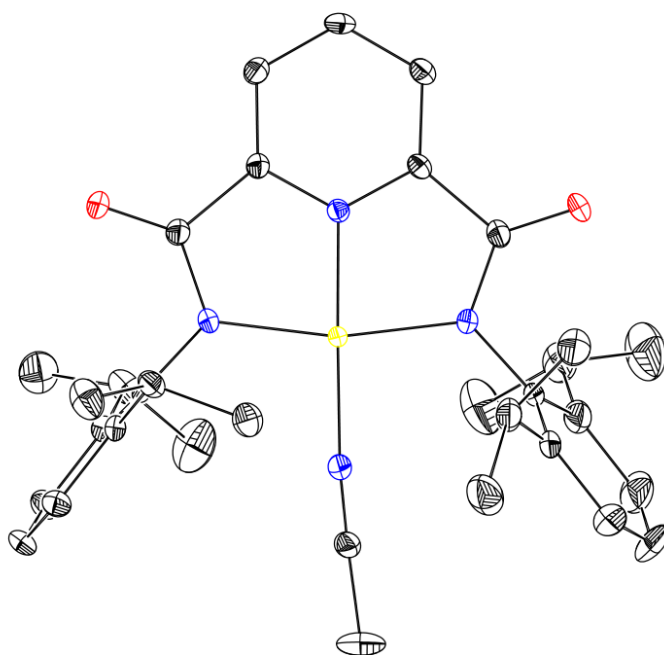


Figure 6.1. ORTEP plots (at 50% probability level) of the X-ray structure **62**. Hydrogen atoms and solvents of crystallisation have been omitted for clarity.

than in those, previously reported, with a d^8 (Ni^{II} , Pd^{II} , Au^{III}) or d^9 (Cu^{II}) electronic structure. It also contributed a further confirmation of the structures of the metastable, d^7 , $[\text{Ni}^{\text{III}}(\text{X})(\text{pyN}_2^{\text{Me}_2})]$ complexes described in chapters 2 to 4, which could not be crystallographically characterised but were identified as square planar on the basis of EPR and EXAFS spectroscopies and DFT calculations.

The stability of the structure in solution was confirmed by the identification in the ESI-MS spectrum of a peak corresponding to $[\mathbf{62} + \text{Na}]^+$. The ^1H NMR spectrum of **62** in CD_3CN (fig. 6.2, top) displayed paramagnetically shifted and broadened signals, as expected for a cobalt(II) complex. Six different signals could be identified, which compares with seven distinct proton environments in the molecule. Interestingly, dissolving **62** in $[\text{D}_6]\text{DMSO}$ yielded a completely different spectrum (fig. 6.2, middle), most likely as an effect of the DMSO acting as a ligand and replacing the CH_3CN (sch. 6.1). This spectrum had sharper signals, whose position and integration were similar to those of the paramagnetic Ni^{II} complexes reported in chapter 4, facilitating their assignment (fig. 6.2).

An important feature was the presence of two distinct signals, with integration equal to 12 protons each, at 9.7 and -10.7. These correspond to the two distinct CH_3 groups of each isopropyl group, which are diastereotopic in the complex. Their environments could

Table 6.1. Average bond distances (Å) and angles (°) for **62**, **56** and **64**.

	62	56	64
M–N _{pyridine}	1.829(2)	1.818(2)	2.112(4)
M–N _{amide}	1.899(2)	1.89(5)	2.103(4)
M–N _{CH₃CN} / Br	1.891(2)	1.862(2)	2.366(1)
M–O _{amide}			2.603(4)
N _{pyridine} –M–N _{amide}	83.1(1)	83.2(2)	78.44(17)
N _{amide} –M–O/N/Cl _{plane}	96.9(11)	96.8(10)	
N _{amide} –M–N _{amide} '	165.9(1)	166.73(7)	
N _{pyridine} –M–O/N/Cl _{plane}	178.5(1)	177.44(7)	
N _{amide} –Zn–Br			108.7(7)
N _{pyridine} –Zn–Br			119(5)
Br–Zn–Br			114.54(4)
τ_4	0.11	0.12	0.86

only be exchanged by rotation around the N–Ar bond, which is free in H₂pyN₂^{*i*Pr₂} but is blocked by coordination to the metal. This effect was also observed in the spectra of the diamagnetic Ni^{II} complexes of pyN₂^{*i*Pr₂}, **56** and **57a** (chapter 5), and can be considered diagnostic of complexation. The magnetic moment of **56** in [D₆]DMSO was determined *via* the Evans method, giving a value of 1.76 μ_B , which is consistent with a single unpaired electron ($S = 1/2$, low spin Co^{II}).

The crystallographic and spectroscopic characterisation of **62** confirmed the formation of a square planar Co^{II} complex. In order to probe its usefulness as a precursor for higher valent (either Co^{III} or Co^{IV}) oxidants, its oxidation and the introduction of oxygen ligands were then investigated. Cyclic voltammetry of **62**, in either acetone or acetonitrile, displayed a reversible redox wave at 0.28 V vs Fc⁺/Fc (fig. 6.3), which can be most likely attributed to a Co^{II/III} transition, accompanied by multiple irreversible oxidation waves starting at 0.9 V (fig. 6.5). From these experiments, one can expect one-electron oxidation of **62** to be feasible, even in the absence of an anionic or multidentate ligand aside from pyN₂^{*i*Pr₂}. In contrast, [Ni^{II}(CH₃CN)(pyN₂^{Me₂})] (**47**) did not display reversible oxidation events (chapter 4): this observation is consistent with the Co^{III} oxidation state being more easily accessible than Ni^{III}.

6.3 Formation of cobalt(II) acetate complexes

The introduction of an [–]OAc ligand proved to be a greater challenge, and attempts at isolating such a product have been so far unsuccessful. In part, this is due to **62** being fairly

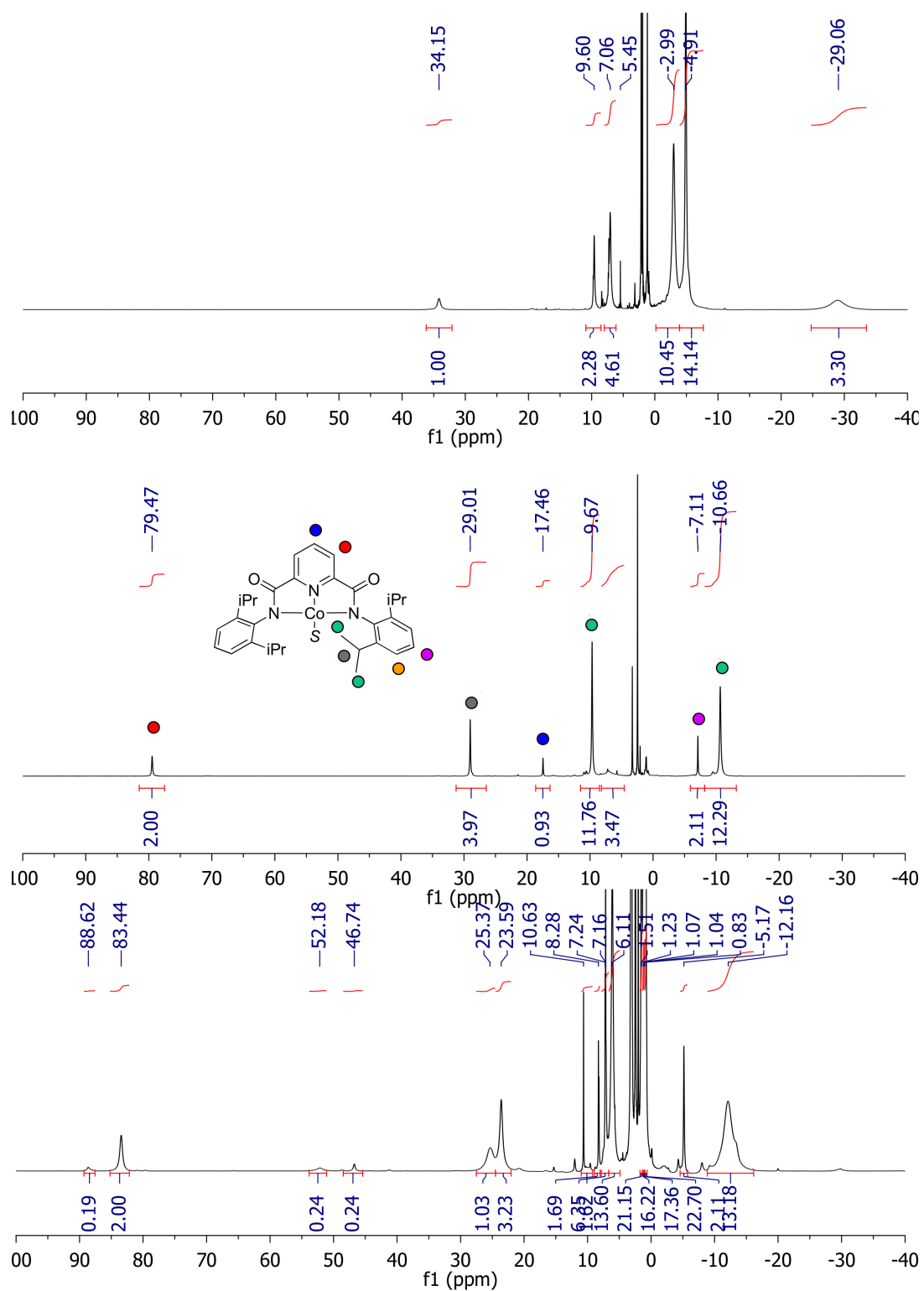


Figure 6.2. ¹H NMR spectra of **62** in CD₃CN (top) and [D₆]DMSO (middle), and after the addition of 1 equivalent of Bu₄NOAc in [D₆]DMSO (400 MHz).

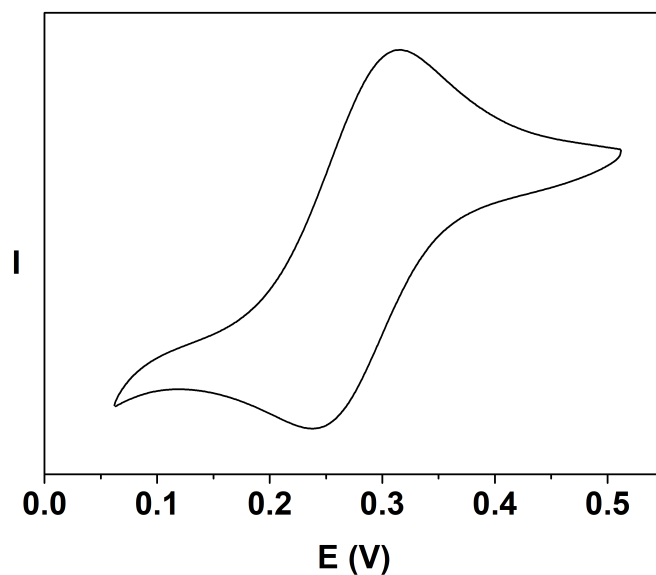


Figure 6.3. Steady state cyclic voltammogram of **62** vs. Fc^+/Fc ; conditions: 0.1 mM (CH_3CN), 0.1 Bu_4NPF_6 , scan rate 0.05 V s^{-1} , room temperature.

sensitive to water, which precludes the use of hydrated Et_4NOAc as a source of acetate. The anhydrous Bu_4NOAc , conversely, made crystallisation of complexes containing the tetrabutylammonium cation more difficult.

However, the formation of a (**62** + Bu_4NOAc) product could be evidenced through spectroscopic techniques. Addition of 1 equivalent of Bu_4NOAc to $[\text{D}_6]\text{DMSO}$ solution of **62** caused substantial shifts in its ^1H NMR spectrum (fig. 6.2, bottom), consistent with the formation of a distinct cobalt complex. A similar reaction was monitored by UV-Vis spectroscopy: **62**, in acetone, on the addition of Bu_4NOAc converted to a new species, with isosbestic points at 450 and 570 nm (fig. 6.4). The voltammogram of **62** in the presence of Bu_4NOAc did not show a simple reversible oxidation wave (fig. 6.5), suggesting the possibility of a more complex behaviour of the $\text{Co}^{\text{III}}\text{-OAc}$ species; nevertheless, its first oxidation event was shifted to a significantly lower potential ($\sim -0.1 \text{ V}$ vs Fc^+/Fc), an expected effect of the coordination of an anionic ligand to the metal centre. In conclusion, these initial experiments showed promise for the preparation of a $\text{Co}^{\text{II}}\text{-OAc}$ complex, to be successively converted into a high valent species. Further synthetic efforts will be expended to this end.

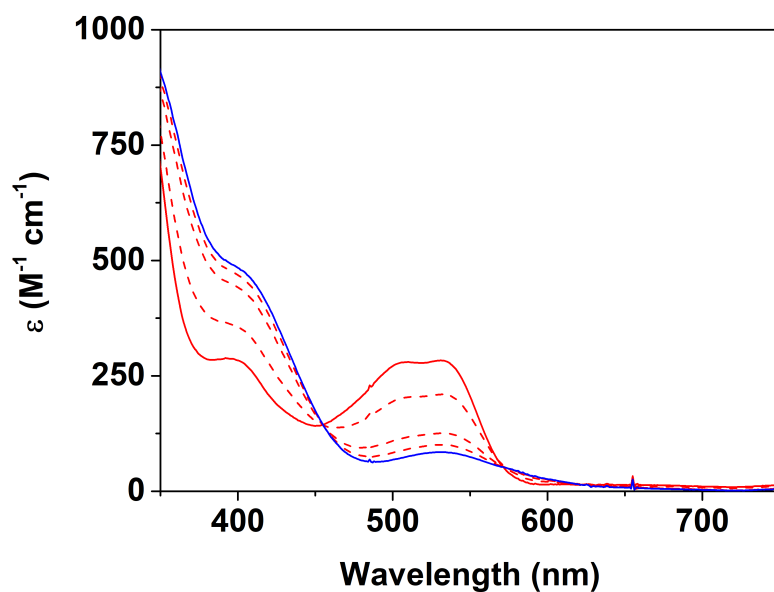


Figure 6.4. Changes in the UV-Vis spectrum of **62** (0.5 mM, acetone, blue trace) on the addition of 1 equivalent of Bu₄NOAc. Red trace: final spectrum.

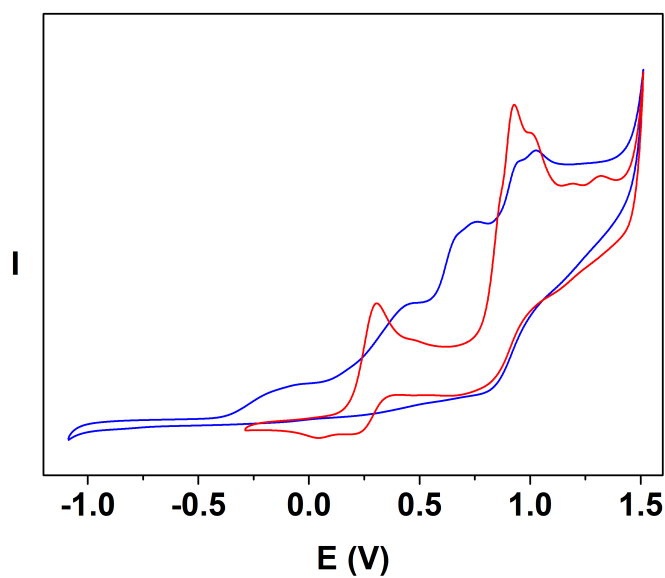
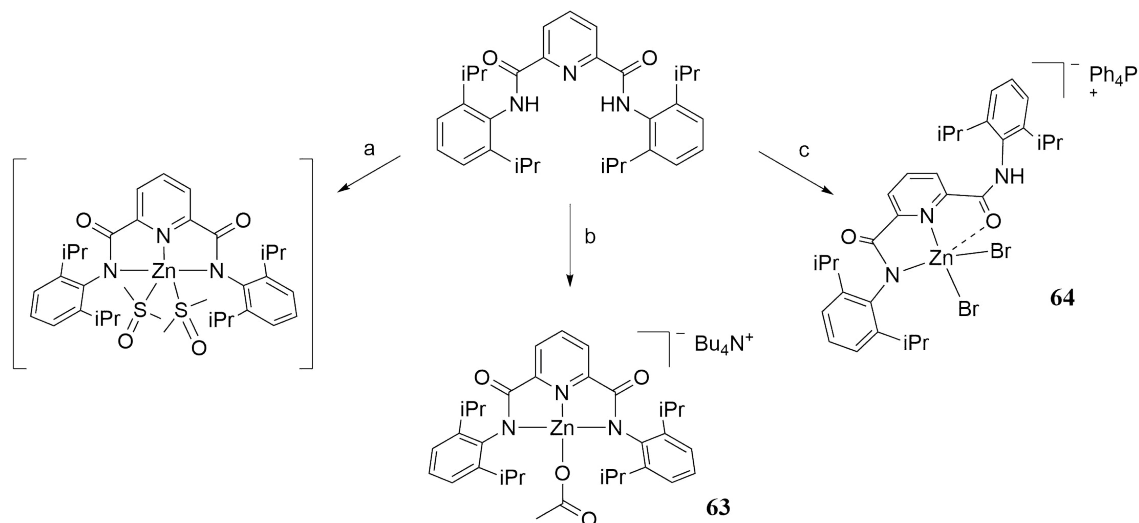


Figure 6.5. Steady state cyclic voltammograms of **62** vs. Fc⁺/Fc, before (blue trace) and after (red trace) the addition of 1.5 equiv. Bu₄NOAc; conditions: 0.1 mM (CH₃CN), 0.1 Bu₄NPF₆, scan rate 0.2 V s⁻¹, room temperature.

6.4 Synthesis and characterisation of zinc(II) complexes

The synthesis of Zn^{II} complexes was successively examined, with interest to their potential redox properties. An issue that transpired in planning their synthesis, is the conflict between the geometry preferences of ligand and metal ion. The $\text{pyN}_2^{\text{R}_2}$ pincer ligands have a planar structure, and small bite angles ($\text{N-M-N} < 90^\circ$), resulting in a strong preference for either square planar coordination, or meridional binding in 5/6 coordinate species. On the other hand, the Zn^{II} ion, because of its d^{10} , closed subshell structure, disfavours square planar coordination: aside from complexes of porphyrinoid and *salen*-type ligands, a search on the Cambridge Structural Database¹³ reveals less than 20 structurally characterised examples. For this reason it should be expected that the $[\text{Zn}^{\text{II}}(\text{pyN}_2^{\text{R}_2})]$ complexes either reach coordination numbers higher than four, or are significantly strained.

Our initial attempts, using methods analogous to those for Ni and Co complexes, that is, the reaction of $\text{H}_2\text{pyN}_2^{\text{iPr}_2}$ with a strong base (BuLi, NaH, KH) and a zinc(II) salt, were unsuccessful, leading to the formation of highly insoluble products. Possibly, these were made of polymeric materials: Erker observed a similar phenomenon,¹ with the formation of $-\text{K}-(\text{Ni}(\text{L}))- \text{K}-$ chains, in which the carbonyl O atoms of $\text{pyN}_2^{\text{iPr}_2}$ functioned as donors to the alkali metal ions.



Scheme 6.2. Synthesis of zinc(II) complexes of $\text{pyN}_2^{\text{iPr}_2}$ a) Et_2Zn (1 eq.), $[\text{D}_6]\text{DMSO}$. b) Bu_4NOAc (1 eq.), Et_2Zn (1 eq.), THF. c) PPh_4Br (1 eq.), Et_2Zn (1 eq.), THF. Recrystallised from CH_2Cl_2 and Et_2O .

Eventually, it was found that $\text{H}_2\text{pyN}_2^{\text{iPr}_2}$ could be reacted with 1 equivalent of diethylzinc (Et_2Zn) in anhydrous DMSO to give a yellow solution (sch. 6.2). The product could not be isolated in the solid state because of the difficulty of removing the solvent and its high

sensitivity to moisture, however, it could be analysed by NMR spectroscopy in $[D_6]DMSO$. Small shifts of peaks compared to $H_2pyN_2^{iPr_2}$, the disappearance of the NH peak at 10.65 ppm, and the splitting of the CH_3 signal from the isopropyl group into two distinct signals unambiguously demonstrated the formation of a complex (appendix A.5).

It was also observed that the addition of another ligand could promote the solubilisation of the zinc(II) complex. Reacting $H_2pyN_2^{iPr_2}$ with Et_2Zn (1 eq.) in THF caused the formation of a precipitate, concomitant with the evolution of gas, but in the presence of Bu_4NOAc (1 eq.) complete dissolution was achieved (sch. 6.2). After removal of the solvent, a light yellow solid was obtained (**63**, 85%). On the basis of ESI-MS, FTIR and NMR spectroscopies, the formula of **63** was assigned as $Bu_4N[Zn(OAc)(pyN_2^{iPr_2})]$. In the first place, a peak at $m/Z = -606$ was detected, corresponding to $[Zn(OAc)(pyN_2^{iPr_2})]^-$ and with isotopic pattern consistent with the proposed formula. The FTIR spectrum did not have peaks at $\tilde{\nu} > 3000\text{ cm}^{-1}$, confirming the absence of N–H bonds and hence that the amide groups were deprotonated. Finally, the ^1H NMR spectrum in CD_3CN (fig. 6.6) showed diagnostic features of complexation as in the DMSO reaction described above, including the disappearance of the NH peak and splitting of the CH_3 doublet. Moreover, a singlet at 0.86 ppm, integrating to 3 protons, was consistent with the coordinated ^-OAc group (comparable with 0.78 ppm in the Ni^{II} analogue **45a**, chapter 3).

Unfortunately, crystals of **63** could not be obtained, so the synthesis of a structural analogue, containing the more rigid tetraphenylphosphonium cation, was attempted. Reaction of $H_2pyN_2^{iPr_2}$ with Et_2Zn (1 eq.) in THF, in the presence of PPh_4Br (1 eq.), yielded a yellow solution in a manner similar to that of **63**. After removal of the THF, the product was redissolved in CH_2Cl_2 and Et_2O was made to slowly diffuse, bringing about the formation of colourless crystals. The analysis by X-Ray diffraction of those revealed a compound of structure $PPh_4[Zn(Br)_2(HpyN_2^{iPr_2})]$ (**64**, fig. 6.7, in which one of the two amide groups was protonated, presumably by adventitious water during the crystallisation process).

64 was a tetrahedral complex ($\tau_4 = 0.86$),¹² with the zinc centre bound to the pyridine group and the deprotonated amide nitrogen of $HpyN_2^{iPr_2}$, and two bromo ligands. The other amide group was rotated so that the diisopropylphenyl group was directed outwards, minimising steric interactions with the zinc centre. Its oxygen atom was oriented towards the Zn atom, at a relatively short distance, which is however not indicative of a bonding interaction: the Zn–O distance = 2.60 Å (table 6.1) was smaller than the sum of the van der Waals radii of Zn and O ($1.39 + 1.52 = 2.91\text{ Å}$),¹⁴ but significantly larger than the sum of their covalent radii ($1.22 + 0.66 = 1.88\text{ Å}$)¹⁵ and at the far end of typical Zn–O bond lengths (1.8–2.5 Å).¹⁶ The rotation of the *N*-aryl-carboxamide arm of the ligand upon protonation, relieving steric encumbrance around the metal, has been previously observed by Tolman in

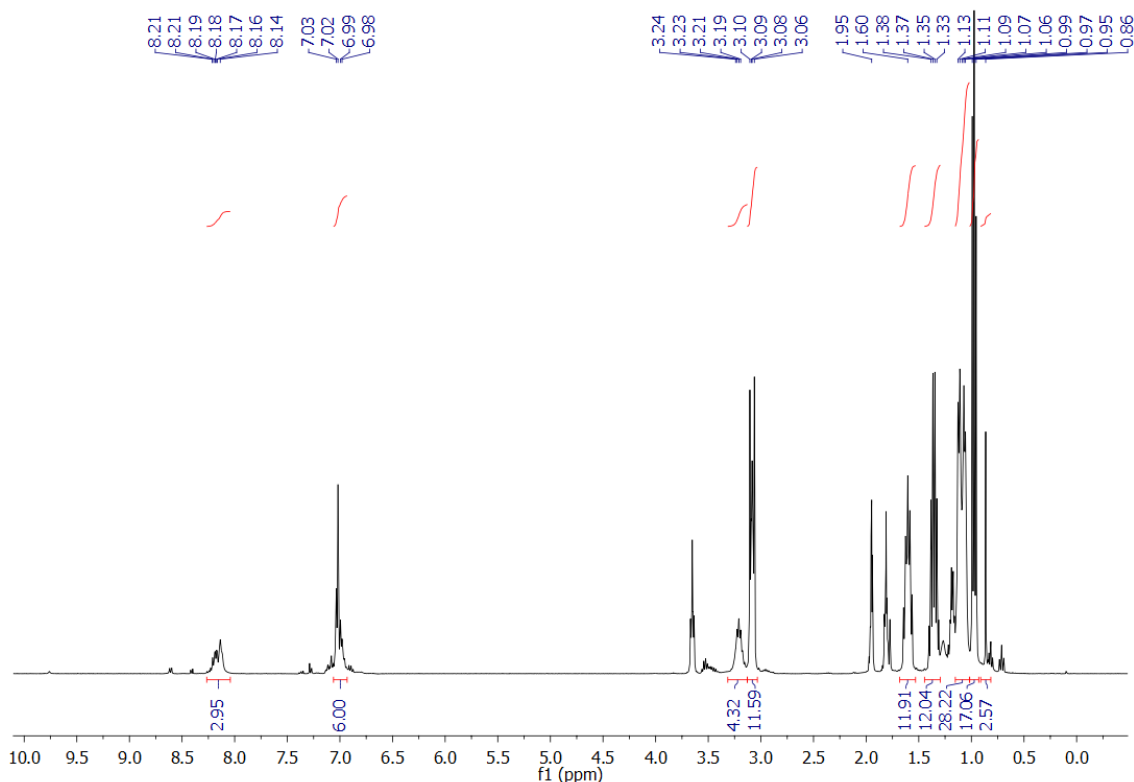


Figure 6.6. ^1H NMR spectrum of **63** (400 MHz, CD_3CN).

copper(II) complexes.⁸ Although **64** did not constitute an effective $[\text{Zn}(\text{X})(\text{pyN}_2^{i\text{Pr}_2})]^-$ type complex as **63**, it demonstrated the formation of a zinc(II) complex of the pyridinedicarboxamide ligand, and work is currently being done towards the structural characterisation of **63**.

6.5 Electrochemical investigation of the zinc(II) acetate complex

The synthesis of **63** constituted an important step in the investigation of the redox properties of the supporting pyridinedicarboxamidate ligand. Cyclic voltammetry was performed on **63**, $\text{H}_2\text{pyN}_2^{i\text{Pr}_2}$, and Bu_4NOAc (as a control experiment) solutions of equal concentration (1 mM), in anhydrous CH_3CN and under an inert argon atmosphere. The protonated ligand alone, $\text{H}_2\text{pyN}_2^{i\text{Pr}_2}$, did not show any redox events in the -0.5 – 1.1 V vs. Fc^+/Fc range (fig. 6.8). In contrast, in the CV of the anionic zinc complex **63**, an intense, irreversible oxidation wave was present at ~ 0.85 V. Bu_4NOAc itself had a similar wave at ~ 0.9 V, which corresponds probably to the oxidation of the $^- \text{OAc}$ anion. One should note

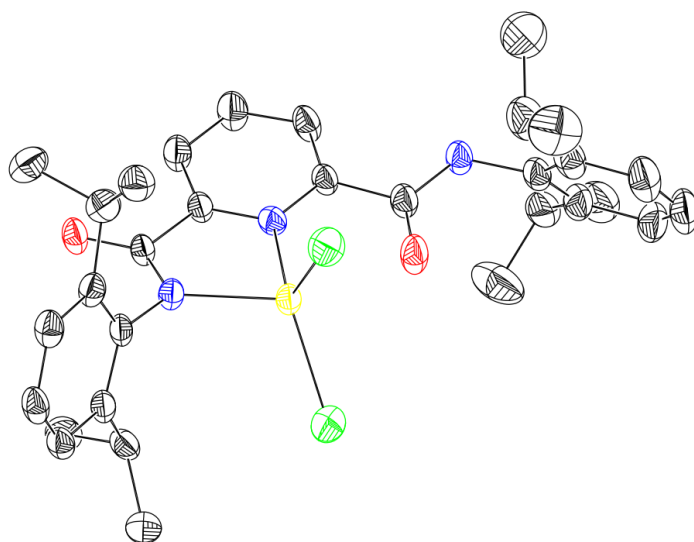


Figure 6.7. ORTEP plots (at 50% probability level) of the X-ray structure **64**. Hydrogen atoms and the counterion Ph_4P^+ have been omitted for clarity.

as well that the $[\text{Ni}^{\text{II}}(\text{CH}_3\text{CN})(\text{py}_2^{\text{Me}_2})]$ compound **47**, also did not show oxidation waves until similarly high potentials (chapter 4).

When compared to the reduction potentials chemical oxidants used for the preparation of Ni^{III} species, these values are rather high (*e.g.* E^0 of magic blue = 0.67 V vs. Fc^+/Fc in CH_3CN ¹⁷). It is unlikely then that a purely ligand-borne oxidation could be affected to yield a stable species. These observations are consistent with the EPR measurements and DFT calculations relative to the Ni^{III} compounds (chapters 2 to 4), which point to electronic structures in which spin density is largely localised on the metal ion. Nevertheless, it will be useful to attempt chemical oxidation, in combination with the use of low temperature techniques, in order to further elucidate the redox behaviour of $\text{H}_2\text{pyN}_2^{\text{iPr}_2}$ and its zinc complexes.

6.6 Conclusions

The work described in this chapter was focussed on expanding the study of pyridinedicarboxamate complexes to other first transition metals, aside from the extensively investigated nickel. A new cobalt(II) complex, **62**, was obtained. It was characterised structurally

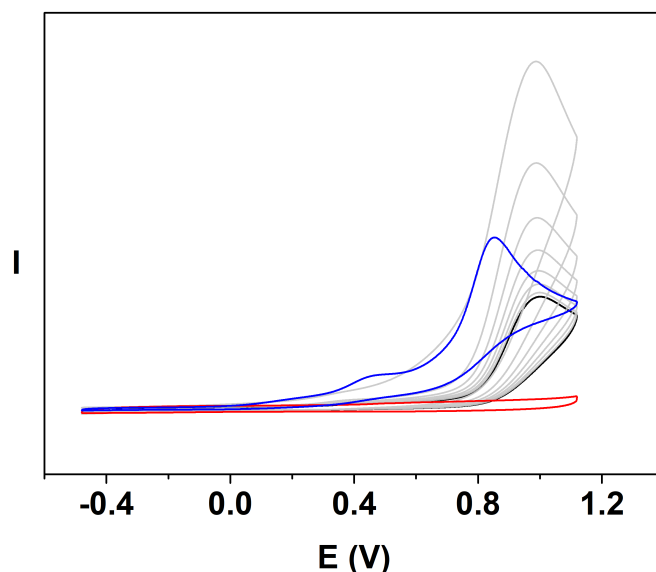


Figure 6.8. Cyclic voltammograms of $\text{pyN}_2^{\text{iPr}_2}$ (red trace), **63** (blue trace) and Bu_4NOAc (black and grey traces). The grey traces are successive, decreasing scans. Conditions: 0.1 mM (CH_3CN), 0.1 Bu_4NPF_6 , scan rate 0.2 V s^{-1} , room temperature, referenced to Fc^+/Fc .

via XRD, as well as ESI-MS, FTIR and NMR spectroscopies. **62** was shown to be a low spin ($S = 1/2$), square planar complex, interestingly isostructural to the corresponding nickel(II) complex **56**: for this reason it constitutes an excellent starting point towards comparative reactivity studies. Conversion of **62** into a $\text{Co}^{\text{II}}\text{--OAc}$ species, and subsequently in a high-valent compound, potentially acting as an oxidant, will be the next step. Although its product yet not structurally characterised, the reaction between **62** and Bu_4NOAc was observed by spectroscopic and voltammetric techniques. Both UV-Vis and ^1H NMR spectroscopies demonstrated the formation of a new species, presumably the target $\text{Co}^{\text{II}}\text{--OAc}$. The CV of **62** showed an oxidation wave at relatively low potential (0.28 V vs Fc^+/Fc), which was further reduced to -0.1 V on binding of ^-OAc . In light of these results, the feasibility of a $\text{Co}^{\text{III}}\text{--OAc}$ species, comparable to the $\text{Ni}^{\text{III}}\text{--OAc}$ **45b** should be anticipated. The synthesis of zinc(II) complexes was also pursued. It was found that metallation of $\text{H}_2\text{pyN}_2^{\text{iPr}}$ yielded highly insoluble products unless a further anionic ligand was introduced. In particular, **63** could be obtained, with an ^-OAc ligand, which was characterised by ESI-MS, FTIR and NMR spectroscopies. Electrochemical investigation revealed that, while $\text{H}_2\text{pyN}_2^{\text{iPr}}$ itself displayed no redox behaviour at $E \leq 1.2 \text{ V}$ vs Fc^+/Fc , **63** afforded irreversible oxidation. This behaviour might have been associated with oxidation of either the $\text{pyN}_2^{\text{iPr}}$ or ^-OAc ligands, and will require to be further probed.

An intriguing feature of the zinc complexes is the contrast between the coordination pref-

erences of the $\text{pyN}_2^{i\text{Pr}_2}$ ligand and the metal centre. Unfortunately, a crystal structure for **63** could not be obtained. Attempts to prepare a bromo- analogue yielded the interesting structure of tetrahedral **64**, in which however one of the carboxamidate groups of $\text{pyN}_2^{i\text{Pr}_2}$ is protonated and does not act as a donor. In conclusion, this synthetic work revealed the versatility of the $\text{pyN}_2^{i\text{Pr}_2}$ ligand, which was capable of binding to d^7 cobalt(II) as well as d^{10} zinc(II). These result open the way to the preparation of new reactive species, which will go on to expand on the work related to the nickel(III) oxidants, and allow to identify trends in the properties and reactivity of M–O–X oxidants.

6.7 Experimental section

Physical Methods

Electronic absorption spectra were recorded on a Hewlett Packard (Agilent) 8453 diode array spectrophotometer (190-1100 nm range) in quartz cuvettes cooled using a liquid nitrogen cooled cryostat from Unisoku Scientific Instruments (Osaka, Japan). ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR analyses were performed on an Agilent MR400 instrument (400.13 MHz for ^1H NMR and 100.61 MHz for $^{13}\text{C}\{^1\text{H}\}$ NMR). ^1H NMR spectra for paramagnetic species were acquired with 64 ms acquisition time and 30 ms relaxation time. Electrospray ionization (ESI) mass spectra were acquired using a Micromass time of flight spectrometer (tof), by direct injection in the mass spectrometry instrument. ATR-FTIR spectra were recorded on a Perkin-Elmer Spectrum 100 Fourier transform infrared spectrometer. Cyclic voltammetry experiments were conducted with a CH Instruments 600E electrochemical analyser, using a glassy carbon working electrode, a platinum wire counter electrode and an Ag/AgNO₃ 0.01 M reference electrode.

Materials and synthesis

All reactions were conducted under an inert Ar atmosphere using standard Schlenk techniques. All solvents and reagents were purchased from commercial sources and used as received, unless otherwise stated. Anhydrous solvents were obtained by sparging with argon, followed by distillation over a drying agent. CaH₂ was used for CH₃CN and CH₂Cl₂; sodium an benzophenone were used for THF and diethylether; B₂O₃ was used for acetone. Anhydrous DMF and DMSO were purchased from Aldrich. *N,N'*-(2,6-diisopropylphenyl)pyridine-2,6-dicarboxamide was prepared according to a reported procedure.¹

Spin State Measurements

The effective magnetic moments ($\mu_{eff.}$) of the Co^{II} complex **62** was measured using the modified Evans method at room temperature.¹⁸ A capillary tube containing [D₆]DMSO (spiked with ~1% protic DMSO) was inserted in the NMR tube containing the solution of the desired compound in the same deuterated solvent. The ^1H NMR spectrum was recorded under standard conditions, and the difference between the paramagnetically shifted and the non-shifted solvent signals was measured. χ_{mol} was calculated using the equation:

$$\chi_{mol} = \frac{3\Delta\nu M}{4\pi c f}$$

in which f is the oscillator frequency (4×10^8 Hz) of the NMR spectrometer, M is the molar mass of the compound (g/mol), c is the concentration (g/mL), and $\Delta\nu$ is the difference in frequency (Hz) between the two signals. Corrections for the diamagnetic contributions of the organic ligands were subtracted using Pascal's constants,¹⁹ and $\mu_{eff.}$ was obtained as:

$$\mu_{eff.} = \sqrt{\frac{3k_B}{N_A\mu_B^2} \chi_{mol} T}$$

in which k_B is the Boltzmann constant, N_A is the Avogadro constant, μ_B is the Bohr magneton and T is the absolute temperature (K).

Synthesis of [Co^{II}(CH₃CN)(pyN₂^{iPr₂})], acetonitrile(*N,N'*-bis(2,6-diisopropylphenyl)-2,6-pyridinedicarboxamido)cobalt(II), **62** – method A

In a Schlenk flask, H₂pyN₂^{iPr₂} (0.330 g, 0.68 mmol) was dissolved in 5 mL of THF. BuLi (0.6 mL of 2.5 M hexanes solution, 1.5 mmol, 2.2 eq.) was added, resulting in immediate formation of a dark red solution. Subsequently, anhydrous CoCl₂ (0.088 g, 0.68 mmol, 1 eq.) was added, and the solution stirred for 1 h at room temperature, resulting in a dark green solution with some precipitate. The solvent was removed *in vacuo*, and CH₂Cl₂ (10 mL) and CH₃CN (1 mL) were added. The mixture turned orange-red over the course of 24 h. After filtration, the solution was concentrated under vacuum and Et₂O was layered on top of the solution. Diffusion of the Et₂O over the course of 7 days caused the formation of block orange-red crystals (0.085 g, 0.15 mmol, 21%), which were separated from some amorphous dark purple material. One of the crystals was analysed by X-ray diffraction.

δH (400 MHz, CD₃CN): 34.2 (1H), 9.6 (2H), 7.1 (4H), -3.0 (12H), -4.9 (12H), -29.1 (4H).
 δH (400 MHz, [D₆]DMSO): 79.5 (2H, 3,5-py), 29.0 (4H, CH(CH₃)₂), 17.5 (1H, 4-py), 9.7 (12H, CH(CH₃)₂), -7.1 (2H, ArH), -10.7 (12H, CH(CH₃)₂).

ESI-MS (*m/z*): Found: 606.2736 ([M + Na]⁺, C₃₃H₄₀CoN₄NaO₂ requires 606.2381).

ν_{max} (ATR-FTIR) /cm⁻¹: 2959 (CH), 2929 (CH), 2867 (CH), 1638s, 1618, 1605, 1461, 1437, 1346s, 986, 837, 801, 773, 767, 745, 685.

λ_{max} /nm: (acetone) 280 (ϵ /M⁻¹ cm⁻¹ 400), 500 (280), 530 (280).

$\mu_{eff.} / \mu_B$ ([D₆]DMSO): 1.76.

Synthesis of [Co^{II}(CH₃CN)(pyN₂^{iPr₂})], acetonitrile(*N,N'*-bis(2,6-diisopropylphenyl)-2,6-pyridinedicarboxamido)cobalt(II), **62** – method B

In a Schlenk flask, H₂pyN₂^{iPr₂} (1.00 g, 2.06 mmol) was dissolved in 80 mL of CH₃CN. KH was added (0.175 g, 4.36 mmol, 2.1 equiv.), resulting in immediate gas evolution

and causing the solution to turn pale yellow. When bubbling ceased, anhydrous CoCl_2 was added (0.275 g, 2.12 mmol, 1 eq.). The solution turned immediately red, with the formation of some precipitate. After stirring for 6 h, the mixture was filtered, and the solvent was removed *in vacuo*. The product was obtained as an orange powder (1.041 g, 2.06 mmol, 86%), and identified by ^1H NMR spectroscopy to be identical to that produced *via* method A.

Reaction of $\text{H}_2\text{pyN}_2^{i\text{Pr}_2}$ with Et_2Zn , NMR scale The reaction was conducted in a screw-lid closed NMR tube, under an inert Ar atmosphere. $\text{H}_2\text{pyN}_2^{i\text{Pr}_2}$ (28.3 mg, 0.058 mmol) was dissolved in 0.75 mL of $[\text{D}_6]\text{DMSO}$. Et_2Zn (60 μL of 1 M hexanes solution, 0.060 mmol, 1 eq.) was added, causing gas evolution and the formation of a yellow solution. A vacuum was gently applied in order to remove the hexanes, the tube was sealed and the NMR spectrum of the product measured.

δH (400 MHz, $[\text{D}_6]\text{DMSO}$): 8.27 (t, $J = 7.9$ Hz, 1H, 4-py), 8.14 (d, $J = 7.9$ Hz, 2H, 3,5-py), 7.06 – 6.91 (m, 6H, ArH), 3.20 (hept., $J = 6.8$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 1.09 (d, $J = 6.8$ Hz, 15H, $\text{CH}(\text{CH}_3)_2$), 1.02 (d, $J = 6.8$ Hz, 9H, $\text{CH}(\text{CH}_3)_2$).

Synthesis of $[\text{Zn}^{\text{II}}(\text{OAc})(\text{pyN}_2^{i\text{Pr}_2})]$, acetato(*N,N'*-bis(2,6-diisopropylphenyl)-2,6--pyridinedicarboxamido)cobalt(II), 63

$\text{H}_2\text{pyN}_2^{i\text{Pr}_2}$ (0.212 g, 0.44 mmol) and Bu_4NOAc (0.132 g, 0.44 mmol, 1 eq.) were dissolved in 4 mL of THF. Et_2Zn (0.5 mL of 1 M hexanes solution, 0.5 mmol, 1.15 eq.) was added, causing gas evolution and the formation of a yellow solution. The solvent was removed *in vacuo*, and the product obtained as a pale yellow solid (0.317 g, 0.37 mmol, 85%).

δH (400 MHz, CD_3CN): 8.41 – 8.00 (m, 3H, pyH), 7.25 – 6.71 (m, 6H, ArH), 3.29 – 3.14 (m, 4H, $\text{CH}(\text{CH}_3)_2$), 3.09 (m, 8H, Bu_4N), 1.69 – 1.53 (m, 8H, Bu_4N), 1.45 – 1.29 (m, 8H, Bu_4N), 1.14 – 1.02 (m, 24H, $\text{CH}(\text{CH}_3)_2$), 0.97 (t, $J = 7.3$ Hz, 12H, Bu_4N), 0.86 (s, 3H, OAc).

ESI-MS (m/z): Found: -606 ($[\text{Zn}(\text{OAc})(\text{pyN}_2^{i\text{Pr}_2})]^-$, $\text{C}_{33}\text{H}_{40}\text{N}_3\text{O}_4\text{Zn}$ requires 606.2310).

ν_{max} (ATR-FTIR) $/\text{cm}^{-1}$: 2958 (CH), 2935 (CH), 2863 (CH), 1669, 1565, 1437, 1377, 1359, 1105, 830, 720s, 689s.

Synthesis of $[\text{Zn}^{\text{II}}\text{Br}_2(\text{HpyN}_2^{i\text{Pr}_2})]\text{PPh}_4$, dibromo(*N,N'*-bis(2,6-diisopropylphenyl)-pyridine- $\kappa\text{N}''$ -2-carboxamide- κN -6-carboxamido- κO)cobalt(II), 64

$\text{H}_2\text{pyN}_2^{i\text{Pr}_2}$ (300 mg, 0.62 mmol) and PPh_4Br (260 mg, 0.62 mmol, 1 eq.) were dissolved in 8 mL of THF. Et_2Zn (0.65 mL of 1 M hexanes solution, 0.65 mmol, 1.05 eq.) was added,

causing gas evolution and the formation of a yellow solution. The solvent was removed *in vacuo*, leaving a pale yellow solid. This was taken up in CH₂Cl₂ (8 mL), and Et₂O was layered on top of the solution. Diffusion of the Et₂O over the course of 7 days caused the formation of a few colourless crystals, which were analysed by X-ray diffraction, ESI-MS ¹H NMR

δ H (400 MHz, [D₆]DMSO): 8.29 (d, J = 7.7 Hz, 2H, 3,5-py), 8.06 (dd, J = 8.0, 7.7 Hz, 1H, 4-py), 7.89 – 7.79 (m, 4H, PPh₄), 7.74 – 7.66 (m, 8H, PPh₄), 7.61 – 7.51 (m, 8H, PPh₄), 7.25 – 7.17 (m, 2H, ArH), 7.11 (d, J = 7.6 Hz, 4H, ArH), 3.08 (hept., J = 6.8 Hz, 4H, CH(CH₃)₂), 1.09 (d, J = 6.8 Hz, 24H, CH(CH₃)₂).

ESI-MS (m/z): Found: -706 ([Zn(Br)₂(HpyN₂^{*i*Pr₂})]⁻, C₃₁H₃₈Br₂N₃O₂Zn requires 471.1331).

X-Ray diffraction methods

Single crystal X-ray data were collected at 100(2) K on a Bruker Apex II CCD diffractometer using graphite-monochromated Mo-K α radiation (λ = 0.71073 Å), an Oxford Cryo-systems Cobra low temperature device and a MiTeGen micromount. Bruker APEX²⁰ software was used to correct for Lorentz and polarization effects. The structures were solved and refined using the Bruker SHELXTL Software Package.^{21,22}

X-ray structure refinement notes

The structure of **62** was refined as a two component twin. A half occupied MeCN molecule in the unit cell was refined with restraints (ISOR), and a 1/5 occupied diethyl ether molecule was refined with restraints (DFIX) and constraints (EADP). One of the phenyl groups in the PPh₄⁺ cation in the structure of **64** is disordered over two positions (60;40%); restraints (DFIX) and constraints (EADP, AFIX) were used to model the disorder.

Table 6.2. Crystal data and structure refinement parameters for **62** and **64**.

	62	64
Empirical formula	C _{34.80} H _{43.50} CoN _{4.50} O _{2.20}	C ₅₅ H ₅₈ Br ₂ N ₃ O ₂ PZn
Formula weight	618.97	1049.20
Temperature	100(2) K	100.01 K
Wavelength	0.71073 Å	1.54178 Å
Crystal system	Tetragonal	Orthorhombic
Space group	P $\bar{4}$	Pna2 ₁
Unit cell dimensions	$a = 19.4751(8)$ Å $\alpha = 90^\circ$ $b = 19.4751(8)$ Å $\beta = 90^\circ$ $c = 8.6325(4)$ Å $\gamma = 90^\circ$	$a = 16.0140(4)$ Å $\alpha = 90^\circ$ $b = 21.1999(5)$ Å $\beta = 90^\circ$ $c = 14.8733(4)$ Å $\gamma = 90^\circ$
Volume	3274.1(3) Å ³	5049.4(2) Å ³
Z	4	4
Density (calculated)	1.256 Mg/m ³	1.380 Mg/m ³
Absorption coefficient	0.562 mm ⁻¹	3.159 mm ⁻¹
F(000)	1314	2160
Crystal size	0.15 x 0.13 x 0.12 mm ³	0.11 x 0.11 x 0.09 mm ³
Theta range for data collection	2.581 to 26.821°	3.459 to 68.322°
Index ranges	$-24 \leq h \leq 24$, $0 \leq k \leq 24$, $-10 \leq l \leq 10$	$-19 \leq h \leq 19$, $-25 \leq k \leq 25$, $-17 \leq l \leq 17$
Reflections collected	6977	60526
Independent reflections	6977 [R(int) = 0.0496]	9257 [R(int) = 0.0595]
Completeness to theta=	26.000° 99.8 %	67.679° 100.0 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.7454 and 0.7056	0.7531 and 0.6406
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	6977 / 40 / 406	9257 / 3 / 563
Goodness-of-fit on F ²	1.021	1.017
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0289, wR2 = 0.0640	R1 = 0.0484, wR2 = 0.1260
R indices (all data)	R1 = 0.0319, wR2 = 0.0653	R1 = 0.0524, wR2 = 0.1307
Largest diff. peak and hole	0.276 and -0.338 e Å ⁻³	1.103 and -0.670 e Å ⁻³

Cyclic voltammetry

CV experiments relative to compound **62** were conducted on 1 mM solutions of in either acetone or CH₃CN, at room temperature, with 0.1 M Bu₄NPF₆ as the support electrolyte. Scan rates of 0.05–0.2 V s⁻¹ were used. Coordination of ⁻OAc was investigated by the addition of 1.5 equivalents of Bu₄NOAc in the same solutions. No substantial differences were observed for any experiment between acetone and CH₃CN solutions. Potentials were referenced to the Fc⁺/Fc couple by addition of an internal ferrocene standard to the solutions.

CV experiments relative to the zinc(II) compounds were conducted on 1 mM solutions of H₂pyN₂^{*i*Pr₂}, Bu₄NOAc or **63** in anhydrous CH₃CN, under an Ar atmosphere, at room temperature, with 0.1 M Bu₄NPF₆ as the support electrolyte. Scan rates of 0.1 V s⁻¹ were used. Potentials were referenced to the Fc⁺/Fc couple by addition of an internal ferrocene standard to the solutions. Addition of one drop of water caused the destruction of **63**, as evidenced by the formation of white precipitate (presumably Zn(OH)₂).

References

- (1) Wasilke, J.; Wu, G.; Bu, X.; Kehr, G.; Erker, G. *Organometallics* **2005**, 24, 4289–4297.
- (2) Huang, D.; Holm, R. H. *J. Am. Chem. Soc.* **2010**, 132, 4693–4701.
- (3) Huang, D.; Makhlynets, O. V.; Tan, L. L.; Lee, S. C.; Rybak-Akimova, E. V.; Holm, R. H. *Inorg. Chem.* **2011**, 50, 10070–10081.
- (4) Wang, Q.-Q.; Day, V. W.; Bowman-James, K. *Chem. Commun.* **2013**, 49, 8042–8044.
- (5) Johnson, M. W.; DiPasquale, A. G.; Bergman, R. G.; Toste, F. D. *Organometallics* **2014**, 33, 4169–4172.
- (6) Donoghue, P. J.; Tehranchi, J.; Cramer, C. J.; Sarangi, R.; Solomon, E. I.; Tolman, W. B. *J. Am. Chem. Soc.* **2011**, 133, 17602–17605.
- (7) Tehranchi, J.; Donoghue, P. J.; Cramer, C. J.; Tolman, W. B. *Eur. J. Inorg. Chem.* **2013**, 2013, 4077–4084.
- (8) Boyce, D. W.; Salmon, D. J.; Tolman, W. B. *Inorg. Chem.* **2014**, 53, 5788–5796.
- (9) Ray, M.; Ghosh, D.; Shirin, Z.; Mukherjee, R. *Inorg. Chem.* **1997**, 36, 3568–3572.
- (10) Luca, O. R.; Crabtree, R. H. *Chem. Soc. Rev.* **2013**, 42, 1440–1459.
- (11) Kaim, W. *Eur. J. Inorg. Chem.* **2012**, 2012, 343–348.
- (12) Yang, L.; Powell, D. R.; Houser, R. P. *Dalton Trans.* **2007**, 955–964.
- (13) Groom, C. R.; Bruno, I. J.; Lightfoot, M. P.; Ward, S. C. *Acta Crystallogr. Sect. B* **2016**, 72, 171–179.
- (14) Bondi, A. *J. Phys. Chem.* **1964**, 68, 441–451.
- (15) Cordero, B.; Gómez, V.; Platero-Prats, A. E.; Revés, M.; Echeverría, J.; Cremades, E.; Barragán, F.; Alvarez, S. *Dalton Trans.* **2008**, 2832–2838.
- (16) Alvarez, S. *Dalton Trans.* **2013**, 42, 8617–8636.
- (17) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, 96, 877–910.
- (18) Evans, D. F.; Jakubovic, D. A. *J. Chem. Soc., Dalton Trans.* **1988**, 2927–2933.
- (19) Bain, G. A.; Berry, J. F. *J. Chem. Educ.* **2008**, 85, 532–536.
- (20) Bruker APEX v2014.11-0, Bruker AXS Inc., Madison, Wisconsin, USA.
- (21) SHELXL-2014, Bruker AXS Inc., Madison, Wisconsin, USA.
- (22) Sheldrick, G. *Acta Crystallogr. Sect. A* **2008**, 64, 112–122.

Chapter 7

Conclusions and Future Work

7.1 Summary and conclusions

The main subjects of this thesis were the preparation, characterisation and study of the oxidative reactivity of high-valent nickel complexes, supported by pyridinedicarboxamidate ligands ($\text{pyN}_2^{\text{Me}_2}$ and $\text{pyN}_2^{\text{iPr}_2}$). I initially discovered that the previously reported complex $[\text{Ni}^{\text{II}}(\text{OCO}_2\text{H})(\text{pyN}_2^{\text{Me}_2})]^-$ (**44a**) could be reacted with a one electron chemical oxidant (magic blue), to form the metastable $[\text{Ni}^{\text{III}}(\text{OCO}_2\text{H})(\text{pyN}_2^{\text{Me}_2})]$ (**44b**, chapter 2). **44b** was prepared at low temperature ($< -40^\circ\text{C}$) and characterised by EPR and XAS spectroscopies, and DFT calculations, confirming its identity as a Ni^{III} species. It was shown that **44b** was competent in the oxidation of several substrates, including those with weak O–H bonds (2,6-DTBP), C–H bonds (BNAH) and PPh_3 . A kinetic isotope effect of 2.1 hinted towards an HAT/PCET type mechanism in the oxidation of 2,6-DTBP. Conversely, BNAH and PPh_3 acted as net two electron reductants, but it could not be ascertained if the reactions proceeded through a single concerted step (hydride transfer from BNAH, oxygen atom transfer to PPh_3) or sequential electron transfer.

In subsequent work, the scope of the investigation was extended by substituting the $^- \text{OCO}_2\text{H}$ ligand with other monodentate O donors ($^- \text{OAc}$ and $^- \text{ONO}_2$, **45-46a**, chapter 3), Cl^- (**48b**) and multidentate N/O ligands (**51-54a**, chapter 4). This involved the development of a widely applicable synthetic method, consisting in the displacement of the actetonitrile in $[\text{Ni}^{\text{II}}(\text{CH}_3\text{CN})(\text{pyN}_2^{\text{Me}_2})]$ (**47**) by the desired ligand. In the crystal structures of the resulting Ni^{II} compounds, the $[\text{Ni}(\text{pyN}_2^{\text{Me}_2})]$ constituted a mostly unvaried structural unit, with the second ligand affecting the coordination around the metal to form either square planar, square pyramidal or pseudo-octahedral complexes. The spin state of the complexes changed from $S = 0$, for the 4-coordinate species, to $S = 1$ for the 5- and 6-coordinate ones. Intriguingly, the ^1H NMR spectra of the high-spin complexes had paramagnetically shifted and broadened signals, but the peaks were sufficiently sharp and their integration accurate enough to allow for their partial assignment.

From these Ni^{II} species, several more Ni^{III} oxidants were prepared and characterised, by oxidation with either magic blue, CAN or hypochlorous acid. Examination of their EPR spectra showed that they all were $S = 1/2$, d^7 Ni^{III} species, but the signal shape was significantly affected by the coordination environment; in particular hyperfine coupling was only observed with $^{35/37}\text{Cl}$ in $\text{Ni}^{\text{III}}\text{--Cl}$, **48b**, and with ^{14}N nuclei in $\text{Ni}^{\text{III}}(\text{bpy})$, **52b** and $\text{Ni}^{\text{III}}(\text{terpy})$ **53b**.

Analysis of their reactivity in the oxidation of phenols demonstrated that electron poor species were the best oxidants, with the highest reaction rates: those with weakly basic ligands, and in particular $^- \text{ONO}_2$ complex **46b**, had the highest reaction rate, while **51b** and **54b** with the strongly electron donating *acac* and 2,6-*dipic* ligands were nearly unreactive.

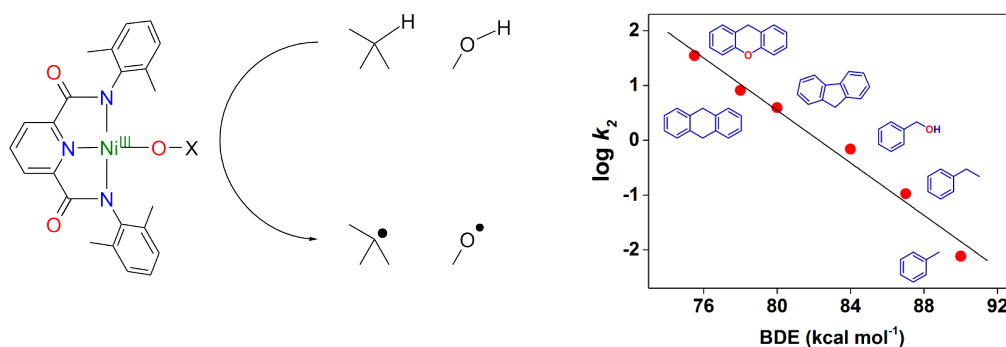


Figure 7.1. Hydrogen atom abstraction reactivity of Ni^{III} complexes (left), and Polanyi relationship between reaction rates and substrate BDE_{C-H} for **45b** (right).

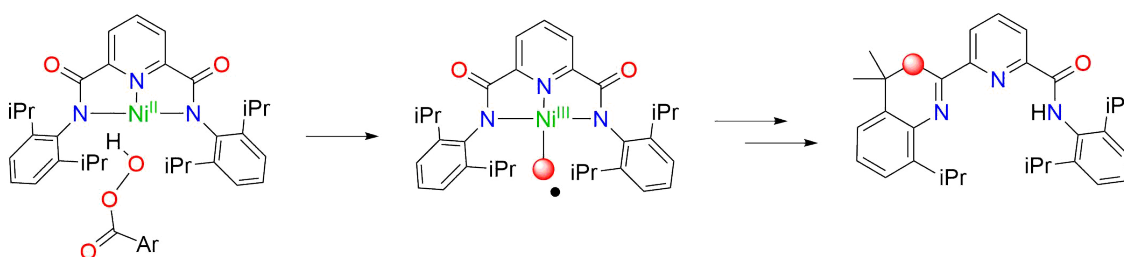


Figure 7.2. Reaction of **56** with *m*-CPBA, forming a transient Ni^{III}-O• species, and the benzoxazine **58** derived from ligand oxidation.

The ⁻OAc complex **45b**, when prepared with NaOCl/AcOH, was stable at 25 °C for more than 10 minutes, allowing to study its reactivity with hydrocarbons, which, compared to phenols, are more sluggish in HAT and PCET reactions. **45b** oxidised a range of hydrocarbons, with BDE_{C-H} values going from 75.5 (xanthene) to 89 kcal/mol (toluene). Kinetic analysis revealed a linear relation between reaction rates and the BDE_{C-H} of the substrates (Bell-Evans-Polanyi relationship, fig. 7.1); together with observed KIEs of 3.0-3.3, this constituted strong evidence of an HAT mechanism. Importantly, the reaction rates were particularly high, surpassing those of most known Mn^{III}-O-X and Fe^{III}-O-X oxidants, and rivalling Fe^{IV}=O and Cu^{III}-OH species which are amongst the fastest known hydrogen atom abstractors. The conclusion can be drawn that M-O-X complexes can engage in reactivity similar to the well known M=O. While several such examples of hydroxo and alkoxo complexes were previously known, the presence of O- ligands such as carboxylates or nitrate is unprecedented. Furthermore, the high reactivity **45b** showed that oxygen adducts of the late transition metals, and in particular nickel, can constitute powerful oxidants.

Unlike the Ni^{III}-O-X compounds, neither species with the Ni^{IV} oxidation state, nor having an oxo ligand, had sufficient stability to be spectroscopically observed, even at low temperatures (≤ -80 °C). Nevertheless, in chapter 5 evidence that a highly reactive intermediate

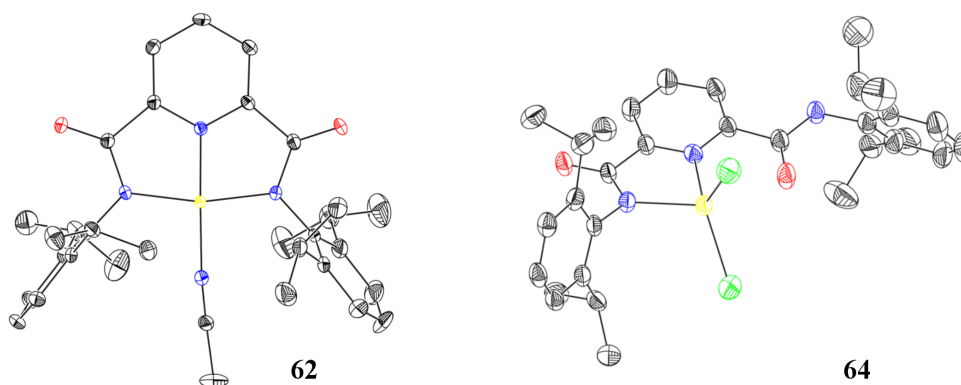


Figure 7.3. Crystal structures of **62** and **64**.

is transiently formed in the reaction of $[\text{Ni}^{\text{II}}(\text{CH}_3\text{CN})(\text{pyN}_2^{\text{iPr}_2})]$ (**56**) with *m*-CPBA was shown. Through the analysis of decay products, isotopic labelling experiments and DFT calculations it was determined that in this reaction, *m*-CPBA acted as a two-electron oxidant, forming a $\text{Ni}^{\text{III}}\text{--O}^\bullet$ species, $[\text{Ni}^{\text{III}}(\text{O}^\bullet)(\text{pyN}_2^{\text{iPr}_2})]$ (fig. 7.2). Interestingly, the principal decay pathway of this intermediate involved hydrogen atom abstraction from a benzylic C–H group of the supporting ligand, which after radical rebound and cyclisation of the resulting benzyl alcohol, led to the formation of an unusual benzoxazine product. A second, longer lived nickel species, $[\text{Ni}^{\text{III}}(\text{O}_2\text{CC}_6\text{H}_4\text{Cl})(\text{pyN}_2^{\text{iPr}_2})]$ (**57b**), resulted from the decay of the $\text{Ni}^{\text{III}}\text{--O}^\bullet$, showing that $\text{Ni}^{\text{III}}\text{--O--X}$ compounds can also form with an exogenous OX ligand source, and not simply by oxidation of the corresponding $\text{Ni}^{\text{II}}\text{--O--X}$.

In the last chapter of the thesis (chapter 6) the coordination of $\text{pyN}_2^{\text{iPr}_2}$ ligand to other metals, specifically cobalt and zinc, was begun to be explored. $[\text{Co}^{\text{II}}(\text{CH}_3\text{CN})(\text{pyN}_2^{\text{iPr}_2})]$ (**62**, fig. 7.3) was obtained, which is interestingly isostructural to **56**. In view of employing it as a precursor to high-valent oxidants, the introduction of an O-donor ligand (OAc^-) was tested: while not structurally characterised, ^1H NMR and UV-Vis spectroscopies demonstrated the formation of a new species, presumably $\text{Co}^{\text{II}}\text{--OAc}$. The oxidation of **62**, and its OAc^- adduct were also assessed in a cyclic voltammetry experiment.

In spite of the pincer ligand $\text{pyN}_2^{\text{iPr}_2}$ and the closed-subshell Zn^{II} ion having conflicting preferences with regards to coordination geometry, complexes $[\text{Zn}^{\text{II}}(\text{OAc})(\text{pyN}_2^{\text{iPr}_2})]^-$ (**63**) and $[\text{Zn}^{\text{II}}(\text{Br})_2(\text{HpyN}_2^{\text{iPr}_2})]^-$ (**64**) could be formed. Of the two, a crystal structure of **64** (fig. 7.3) was obtained, which revealed a tetrahedral zinc centre, with one of the amide groups of $\text{pyN}_2^{\text{iPr}_2}$ protonated and not involved in binding to the metal. Following their successful synthesis, the reactivity and redox properties of cobalt and zinc compounds will be studied, especially in relation to those of nickel.

7.2 Future work

The results presented in this thesis leave several avenues to be explored, in order to further the understanding of the high-valent oxidants examined.

1) Species of the type $\text{Ni}^{\text{III}}\text{--O--X}$, as well as a few other analogous Ni^{III} compounds, have been prepared and extensively studied. The reaction of **45b** with hydrocarbons was shown unambiguously to proceed through an HAT mechanism. The oxidation of other substrates, however, might involve more complex modes of reactivity: for example, anomalous behaviour in the oxidation of phenols by **53b** (which was conducted in methanol), or in general for the oxidation of those substrates which can act as either $\text{H}^\bullet$ or H^- donors (*i.e.* BNAH and *N*-methyldihydroacridine), was observed. Other intriguing questions are whether the relatively low KIE values observed in both C–H and O–H bonds oxidations can be explained, and what is the effective locus of protonation when a hydrogen atom is transferred to the Ni^{III} complex (*i.e.* competition between different atoms in the O- ligand, and the N/O atoms in the supporting $\text{pyN}_2^{\text{R}_2}$ ligand).

An important tool will be the in-depth investigation, and comparison, of the reactivity of compounds **51–54b** which, thanks to their different O/N ligands (*e.g.* *acac*, *bpy*, *terpy*) will allow to elucidate which characteristics are important for the oxidative reactivity. Furthermore, the structural characterisation of these compounds can be completed with techniques such as XAS and DFT, to complement our EPR and UV-vis spectroscopic analyses. Theoretical tools, *i.e.* DFT calculations, will be fundamental for a full comprehension of the reaction mechanisms of Ni^{III} compounds.

2) An interesting question is whether even more powerful oxidants could be accessed by further oxidation to Ni^{IV} . The work conducted using 2-electron oxidants, and in particular *m*-CPBA, showed that such a species can be formed. However, it could not be intercepted and observed spectroscopically, but only got indirect evidence, due to its high instability. It will be necessary to explore new conditions that allow the observation of Ni^{IV} species, including for example using different solvents and oxidants, and lower temperatures. However, it seems likely that sufficient stabilisation of a Ni^{IV} cannot be achieved with the $\text{pyN}_2^{\text{Me}_2}$ or $\text{pyN}_2^{\text{iPr}_2}$ ligands. The formation of the benzoxazine **58**, in the reaction of **56** with *m*-CPBA, showed that the benzylic C–H groups represent a vulnerability, as their $\text{BDE}_{\text{C–H}}$ is relatively weak. Eliminating this will be necessary in order to isolate highly reactive species: for example, by substituting the methyl or isopropyl substituents with phenyl or *tert*-butyl groups. A second useful modification of the ligand would be to make it more electron-donating, so as to stabilise the higher oxidation state: this could be achieved either by the introduction of electron-donating substituents on the aromatic

ring, or even by a more radical change to introduce a further anionic donor (*e.g.* pyrrolide instead of pyridine).

3) Finally, the central motivation behind my research in nickel compounds was the hypothesis that oxidants based on the late first-row transition metals (Co, Ni and Cu) would possess a greater oxidising power, and possibly new reactivity in comparison to those based on iron and manganese. In this view, it will be highly interesting to obtain a series of compounds with different central metals, going from iron to copper, but similar coordination environment. Analysis of the literature, together with the initial results in the synthesis of cobalt complexes, is promising in suggesting that this may be achievable with the $\text{pyN}_2^{\text{iPr}_2}$ ligand. Tolman has demonstrated that $\text{Cu}^{\text{II/III}}$ complexes of $\text{pyN}_2^{\text{iPr}_2}$ can be relatively easily accessed, and parallel work is being conducted in my group on Cu–OAc species. The Co^{II} complex **62** was prepared, which is an excellent starting material. Following this result, it will be converted to potential oxidising species by the introduction of O ligands, particularly OAc^- , and oxidising it to Co^{III} . Moreover, the Co^{IV} state will also be explored, either by sequential, one-electron oxidation of $\text{Co}^{\text{II}}\text{--O--X}$ species, or by reacting **62** with reagents capable of transferring oxygen atoms (*e.g.* peroxyacids such as *m*-CPBA, iodosoarenes, peroxides and amine *N*-oxides). Ideally, one would be able to isolate an oxo ($\text{Co}^{\text{IV}}\text{=O}$) or oxyl ($\text{Co}^{\text{III}}\text{--O}^\bullet$) complex, similar to the transient $\text{Ni}^{\text{III}}\text{--O}^\bullet$.

Once the high valent cobalt, copper and iron complexes will have been prepared and characterised, a comparative study of their oxidative reactivity will be done, using methods analogous to those employed for the Ni^{III} species. These will include reacting them with hydrocarbons and other substrates, performing kinetic analysis and examination of the reaction products, so as to garner an understanding of the effect that the different central metal has on oxidising power and other properties of the compounds.

The synthesis of zinc complexes was also pursued, although it is not expected to be able to form higher valent complexes from them. The rationale was to be able to observe the potential redox behaviour of the $\text{pyN}_2^{\text{iPr}_2}$ ligand, independently of a redox active metal centre. The results so far have been inconclusive, in part due to difficulties in obtaining crystal structure for the compounds. Further synthetic efforts will be expended to obtain and characterise $[\text{Zn}(\text{OX})(\text{pyN}_2^{\text{iPr}_2})]$ complexes, and subject them to either electrochemical and chemical means of oxidation.

Appendix A

A.1 Chapter 2

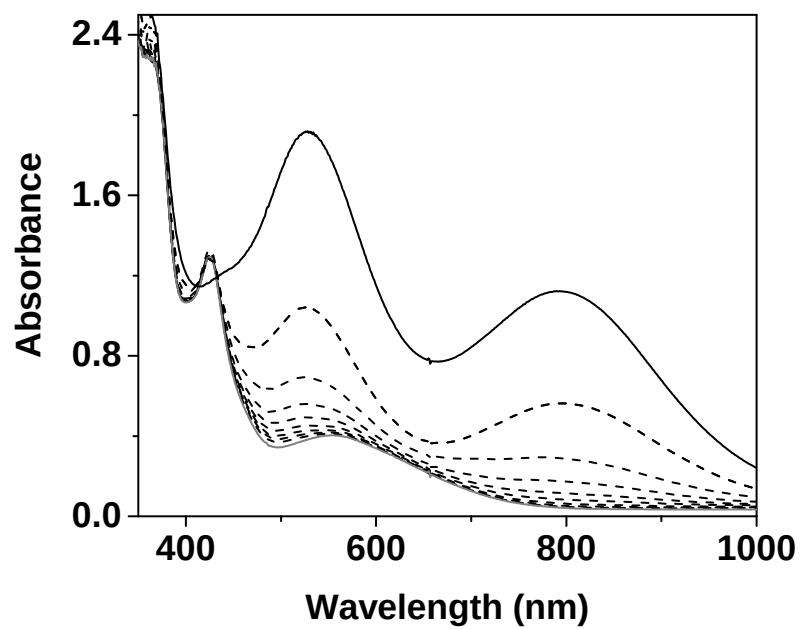


Figure A.1. UV-Vis spectral changes in the reaction of **44b** (solid black trace) with 100 equivalents of 2,6-DTBP at -40 °C in acetone.

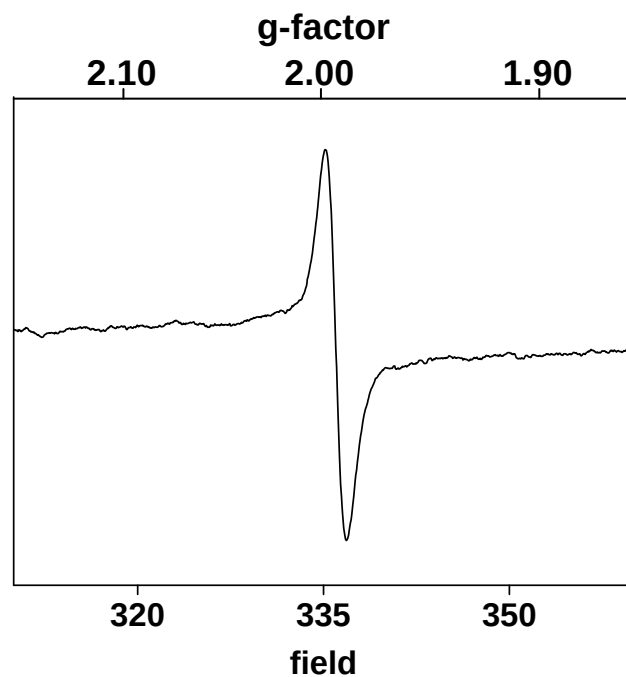


Figure A.2. X-band EPR spectrum of the frozen post-reaction mixture from the reaction between **44b** and 2,6-DTBP. The signal at $g = 2.00$ is indicative of a phenoxyl radical. Measured at 113 K; microwave power = 31.6 mW; modulation amplitude = 0.5 mT.

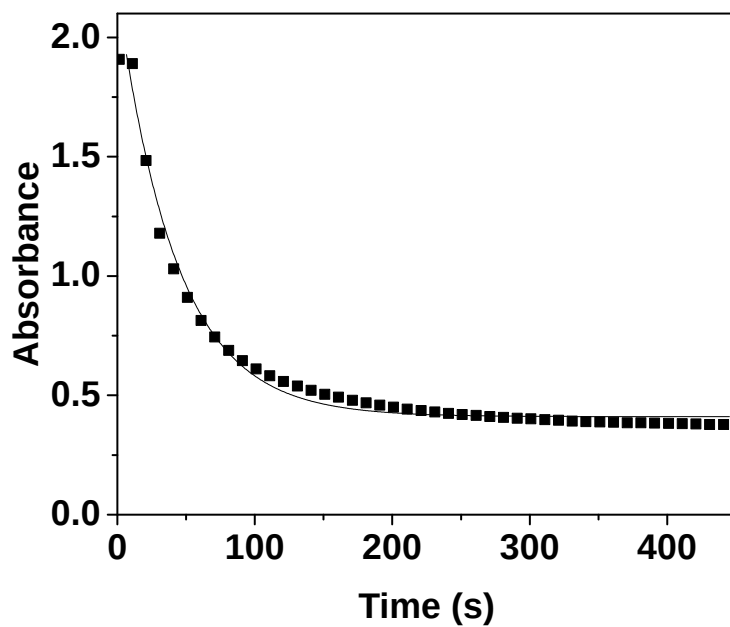


Figure A.3. Plots of absorbance at 520 nm versus time during the reaction between **44b** and 100 equivalents of 2,6-DTBP at $-40\text{ }^{\circ}\text{C}$ in acetone.

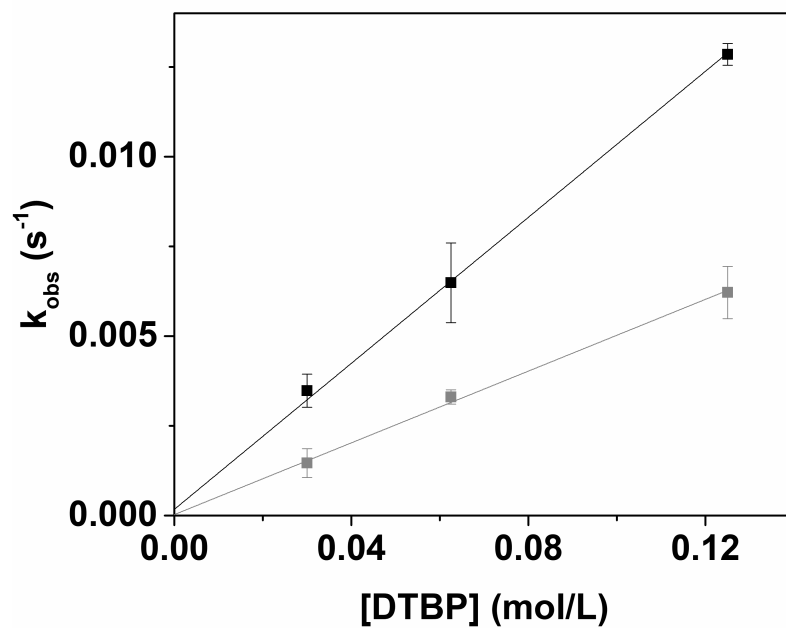


Figure A.4. Plots of k_{obs} versus [2,6-DTBP] determined for the reaction between **44b** and 2,6-DTBP (black), and for the reaction between **44b** and 2,6-DTBP-*d* (grey), at -40 °C in acetone.

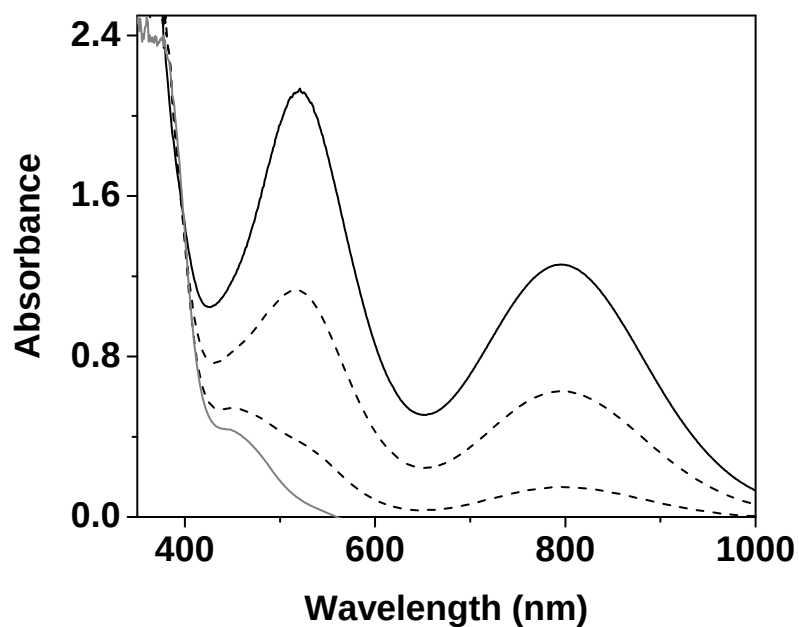


Figure A.5. UV-Vis spectral changes in the reaction of **44b** (solid black trace) with 1 equivalent of BNAH at -80 °C in acetone.

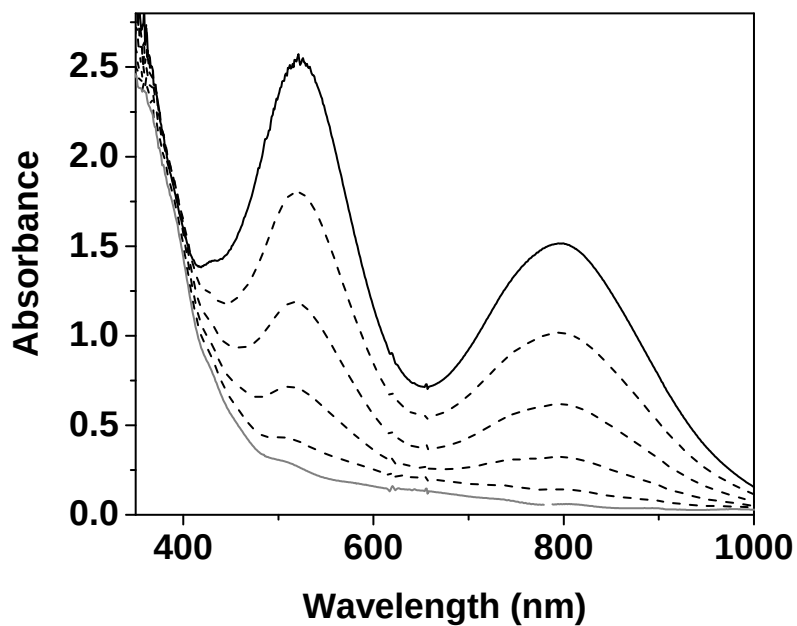


Figure A.6. UV-Vis spectral changes in the reaction of **44b** with 50 equivalent of triphenylphosphine at -80 °C in acetone.

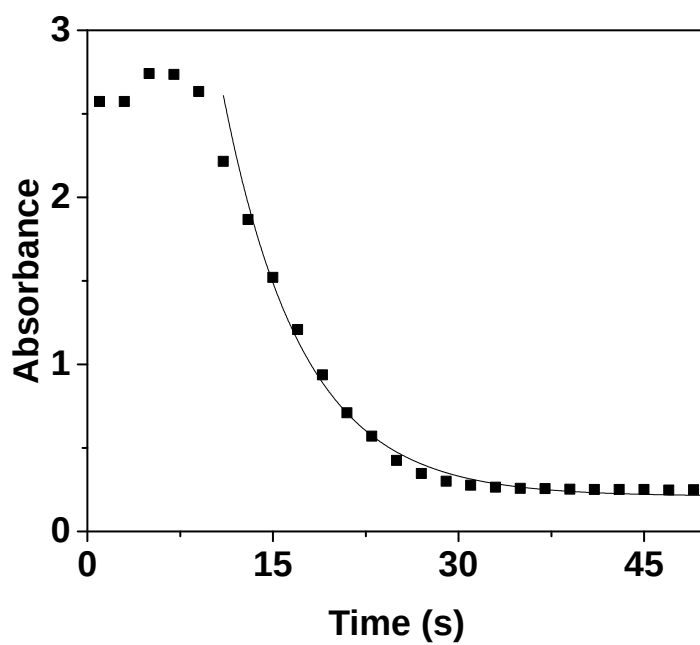


Figure A.7. Plot of absorbance at 520 nm versus time during the reaction between **44b** and 50 equivalents of PPh₃ at -80 °C in acetone.

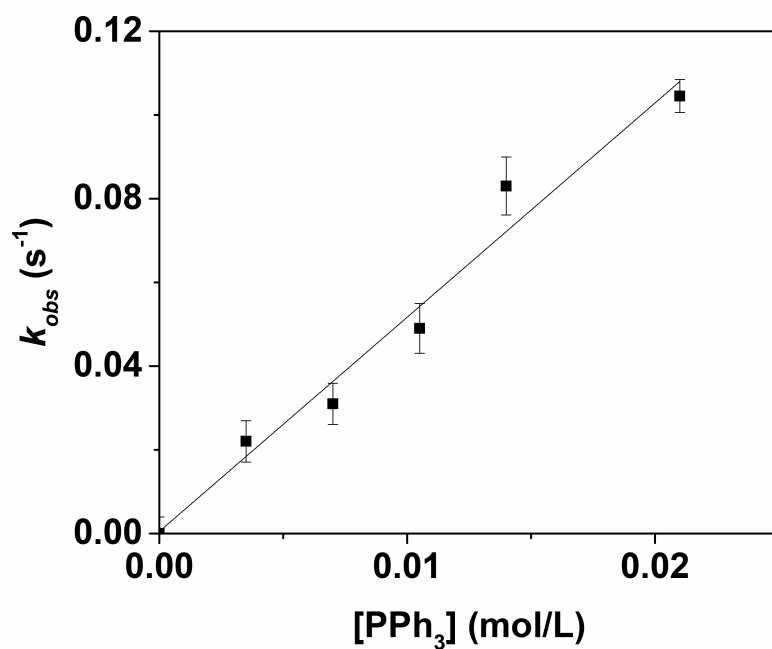


Figure A.8. Plot of k_{obs} versus $[\text{PPh}_3]$ determined for the reaction between **44b** and triphenylphosphine.

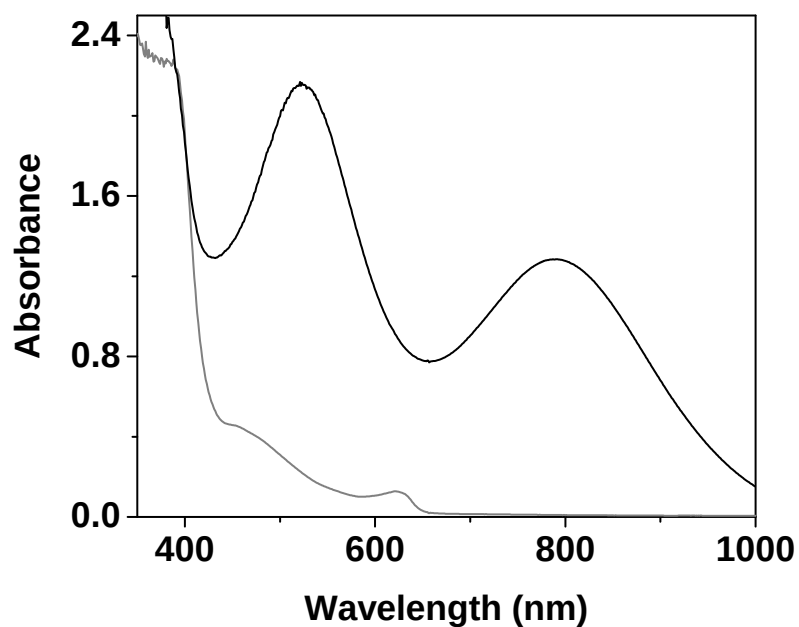


Figure A.9. UV-Vis spectral changes in the reaction of **44b** with one equivalent of ferrocene at -80°C in acetone.

A.2 Chapter 3

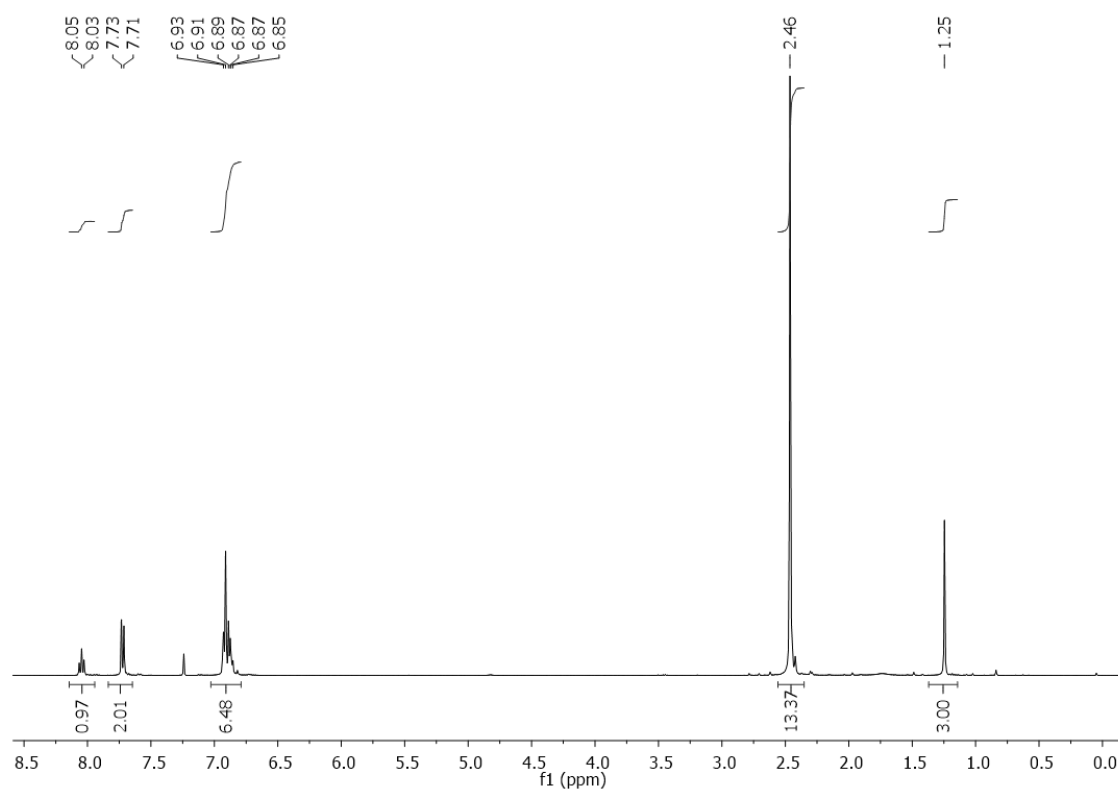


Figure A.10. ¹H NMR spectrum of **47** (400 MHz, CDCl₃).

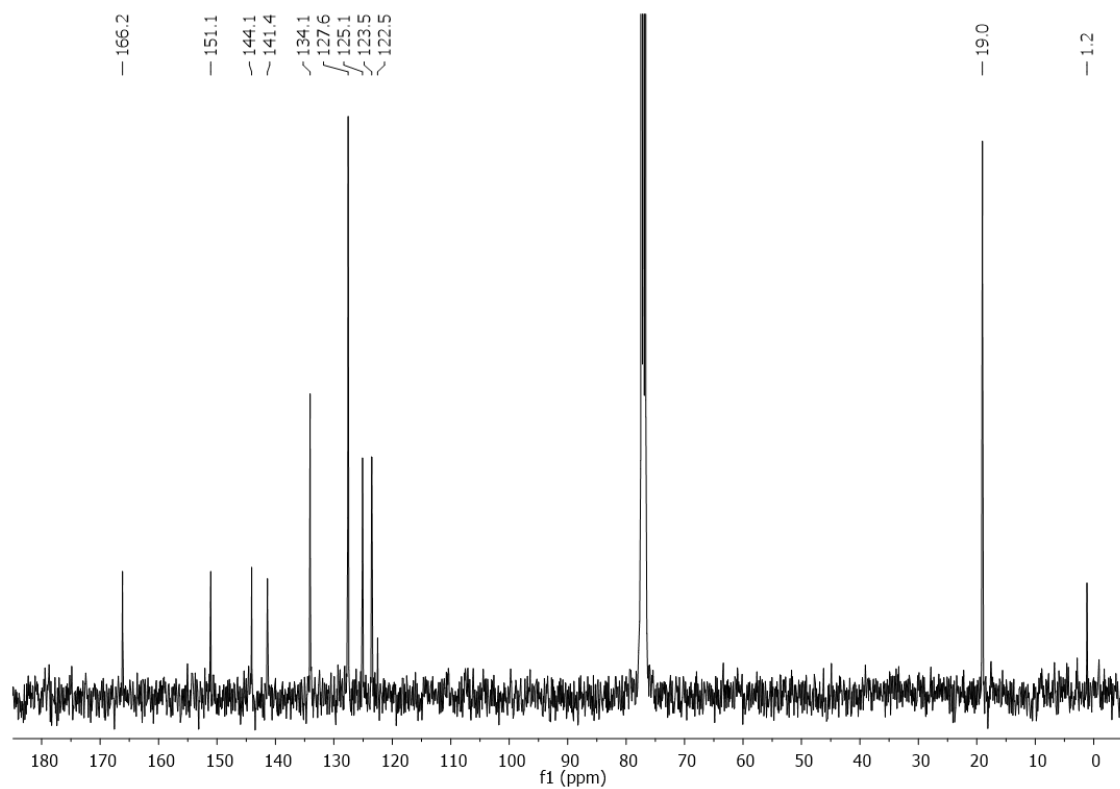


Figure A.11. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **47** (101 MHz, CDCl_3).

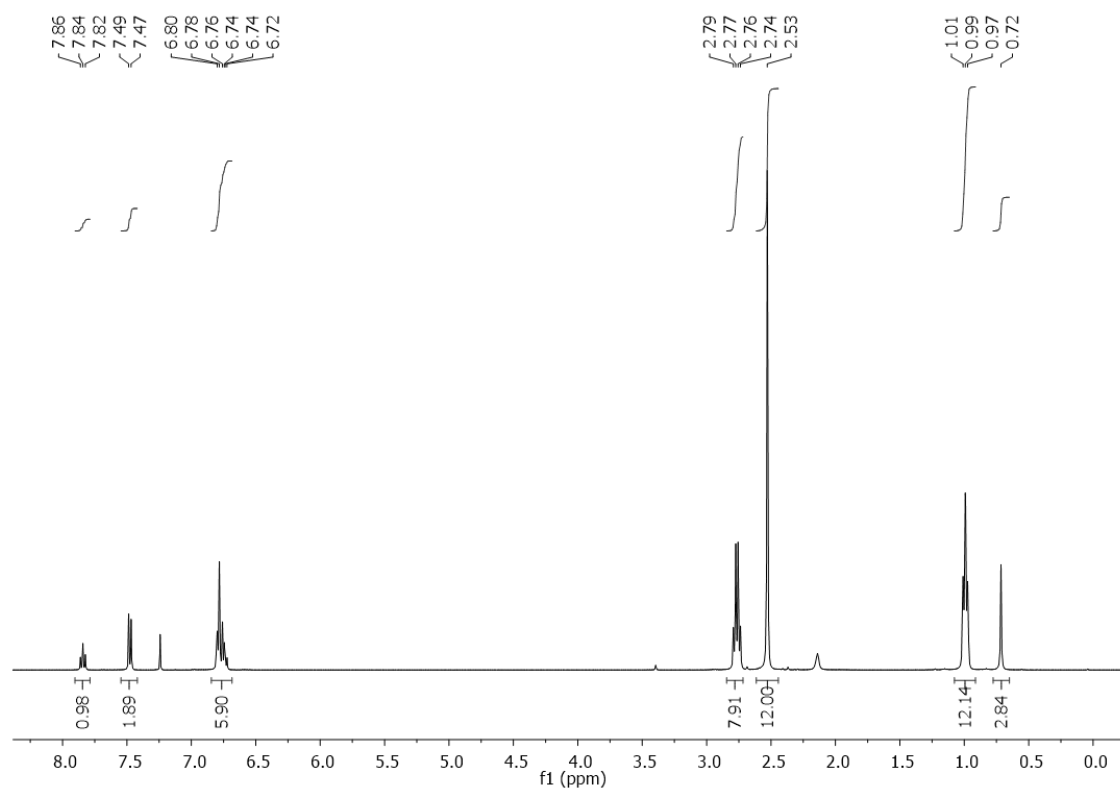


Figure A.12. ^1H NMR spectrum of **45a** (400 MHz, CDCl_3).

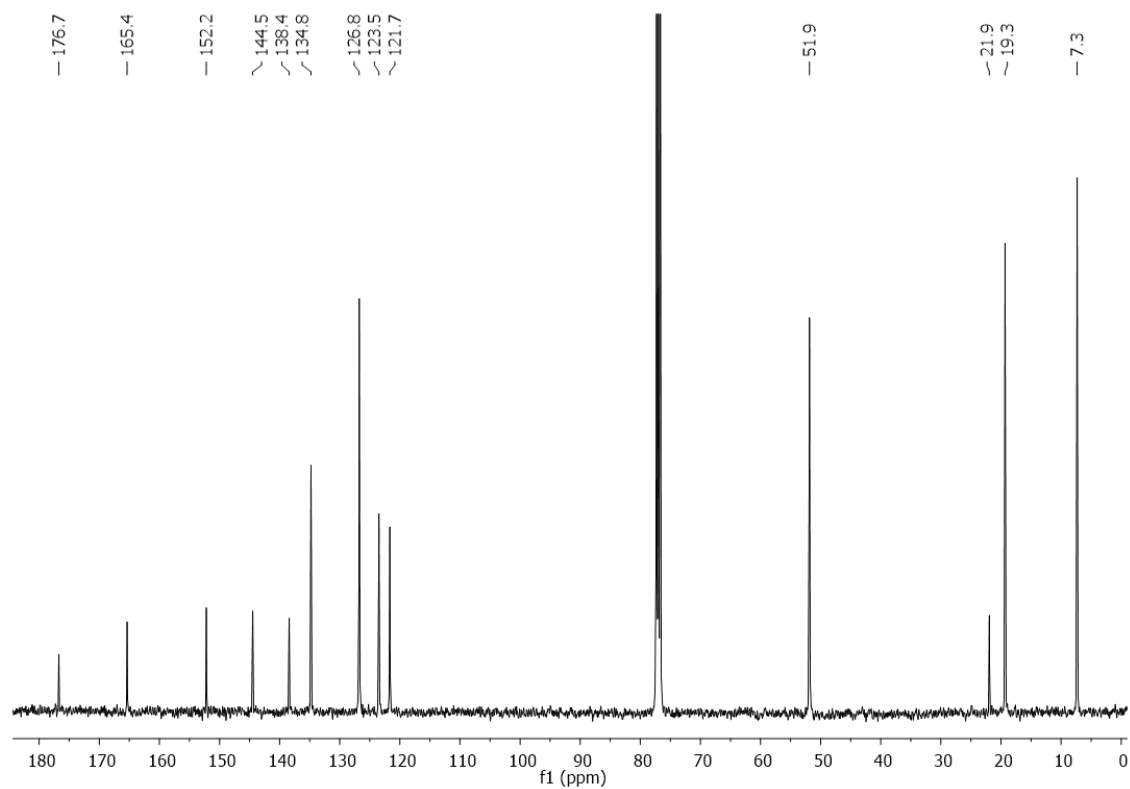


Figure A.13. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **45a** (101 MHz, CDCl_3).

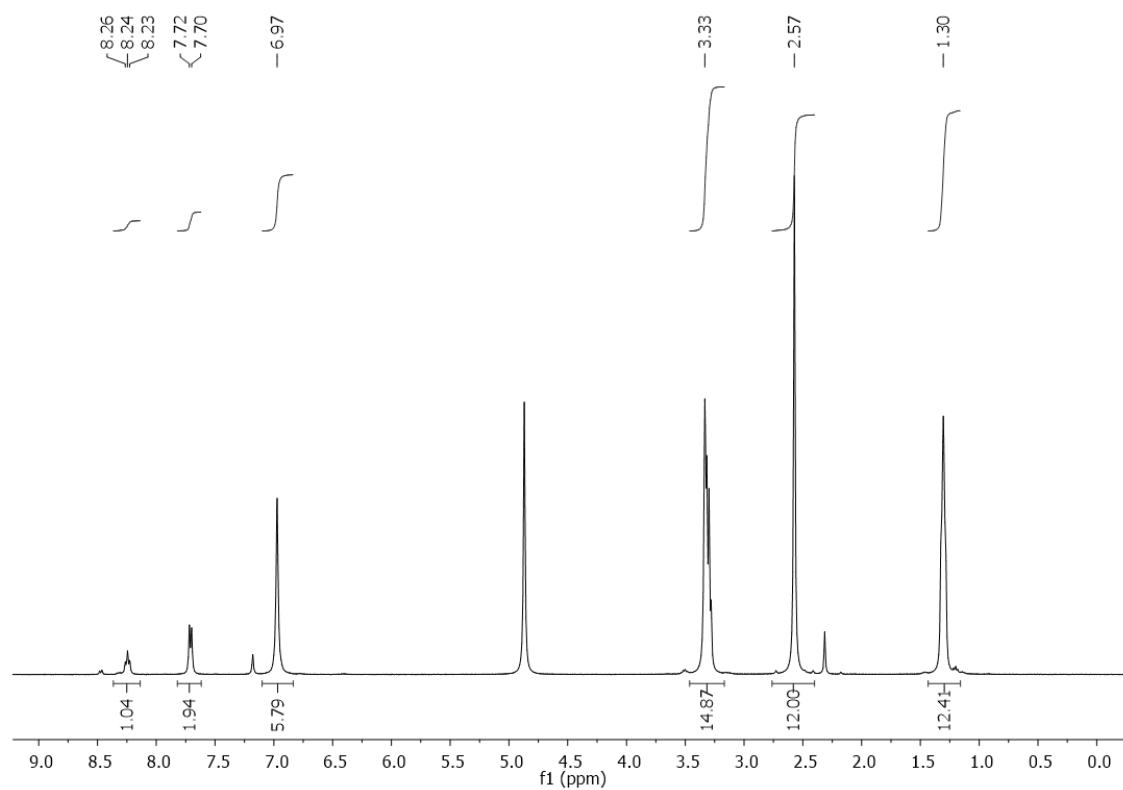


Figure A.14. ^1H NMR spectrum of **46a** (400 MHz, CD_3OD).

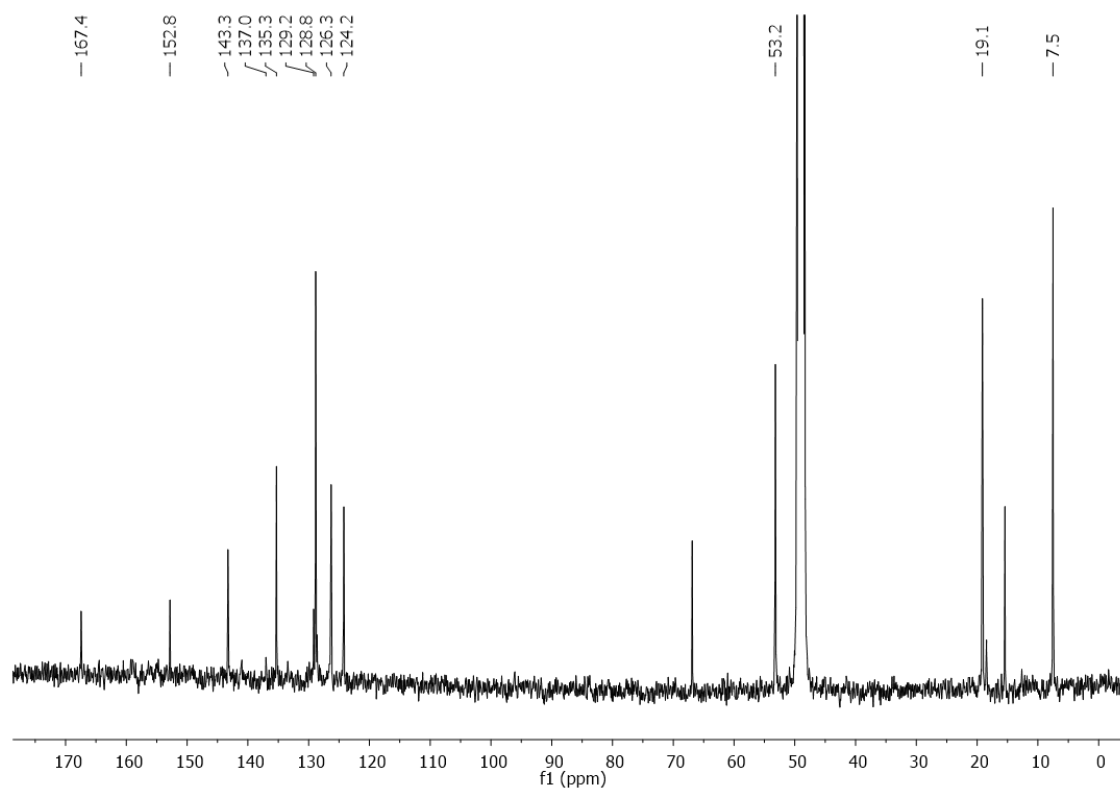


Figure A.15. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **46a** (101 MHz, CD_3OD).

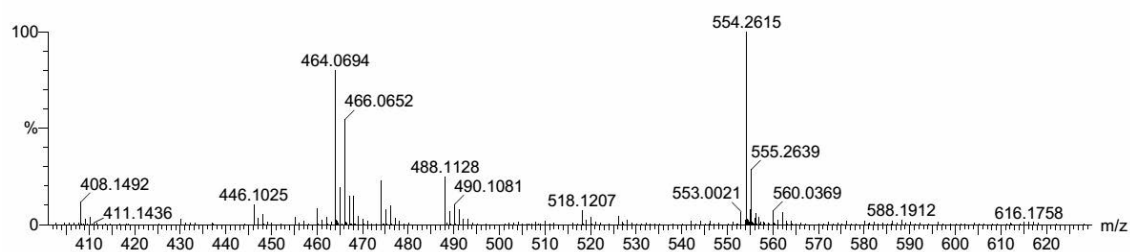


Figure A.16. Positive mode ESI MS spectrum of **47**.

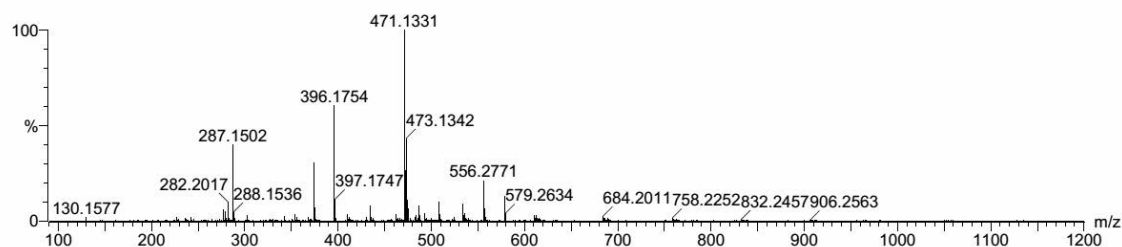


Figure A.17. Negative mode ESI MS spectrum of **45a**.

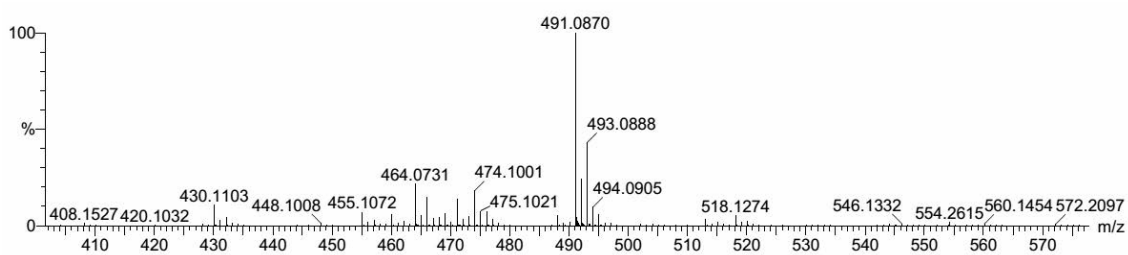


Figure A.18. Negative mode ESI MS spectrum of **46a**.

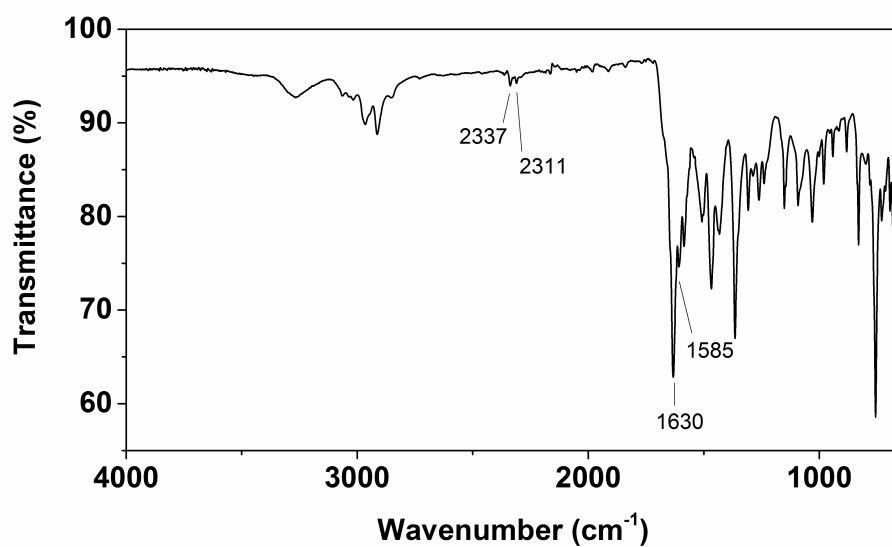


Figure A.19. ATR-FTIR spectrum of **47**.

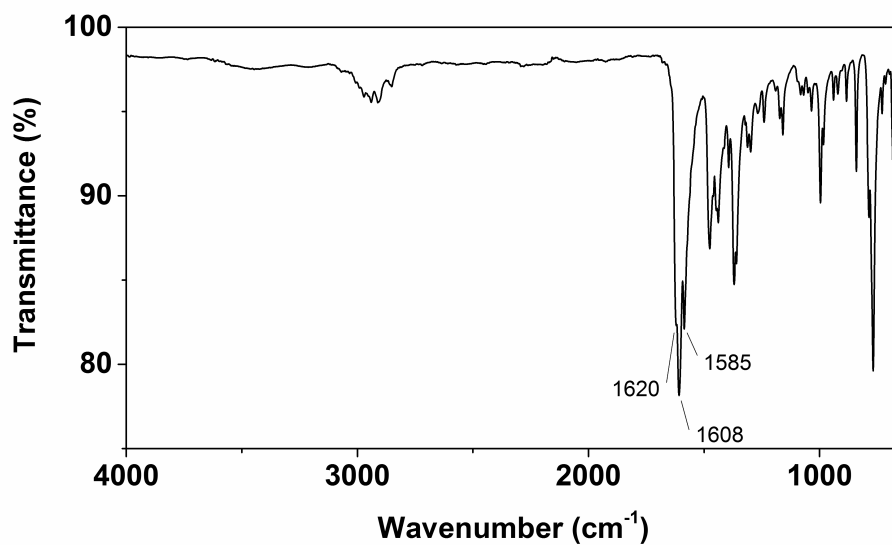


Figure A.20. ATR-FTIR spectrum of **45a**.

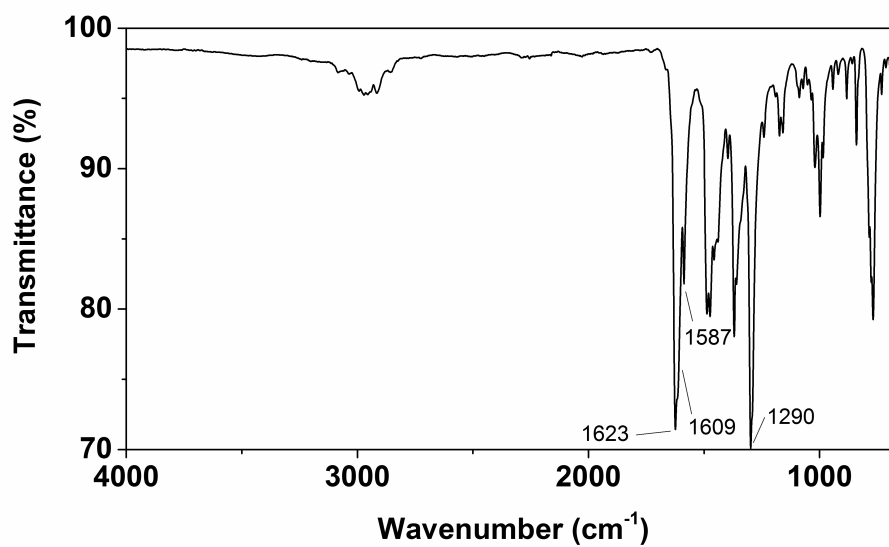


Figure A.21. ATR-FTIR spectrum of **46a**.

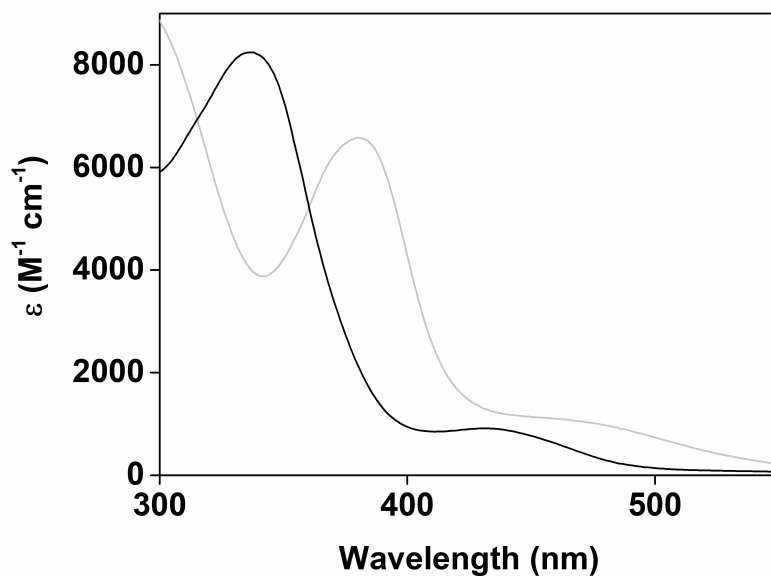


Figure A.22. Electronic absorption spectra of **45a** (black trace) and **47** (grey trace) in acetonitrile.

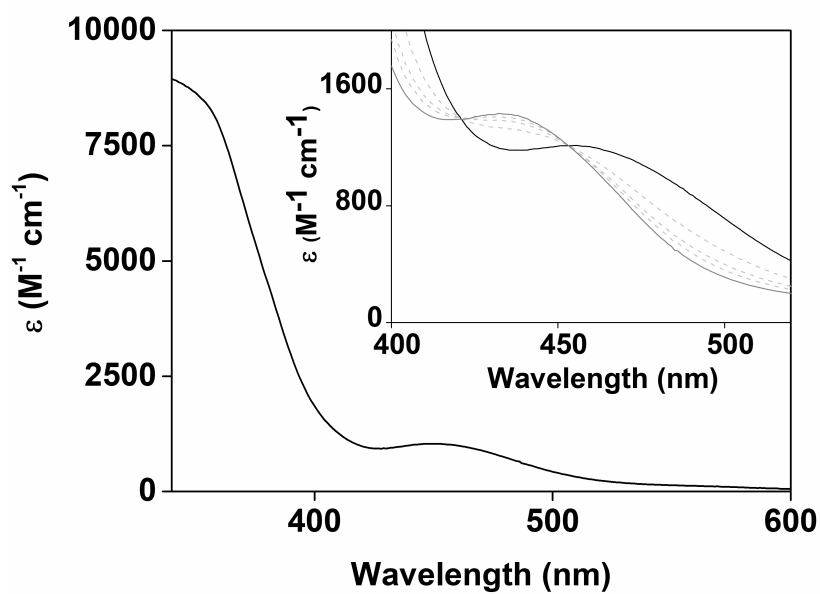


Figure A.23. Electronic absorption spectrum of **46a** (black trace) in acetone; inset: changes upon titration with acetonitrile (325 equivalents increments, up to 1300 eq., grey trace).

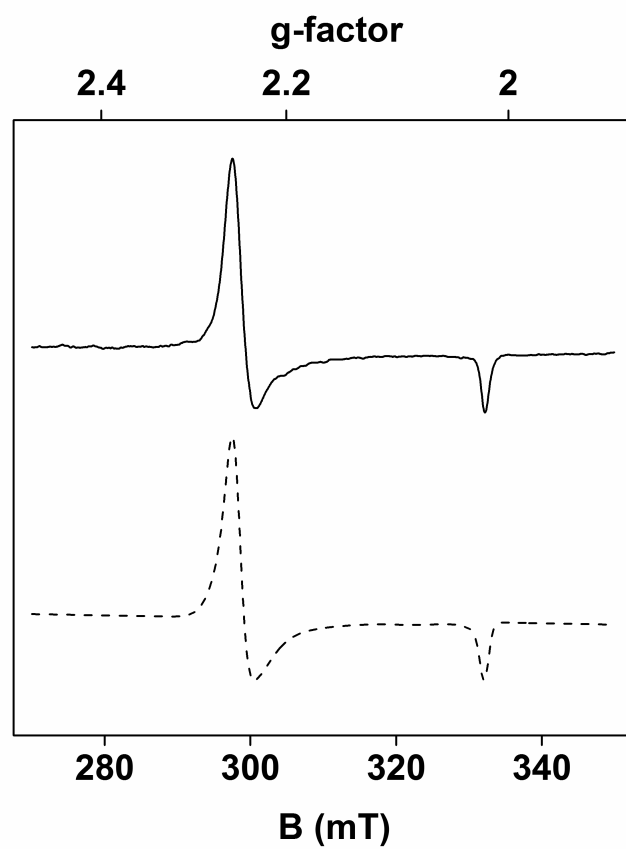


Figure A.24. Experimental (solid trace) and simulated (dashed trace) EPR spectra of **44b**.

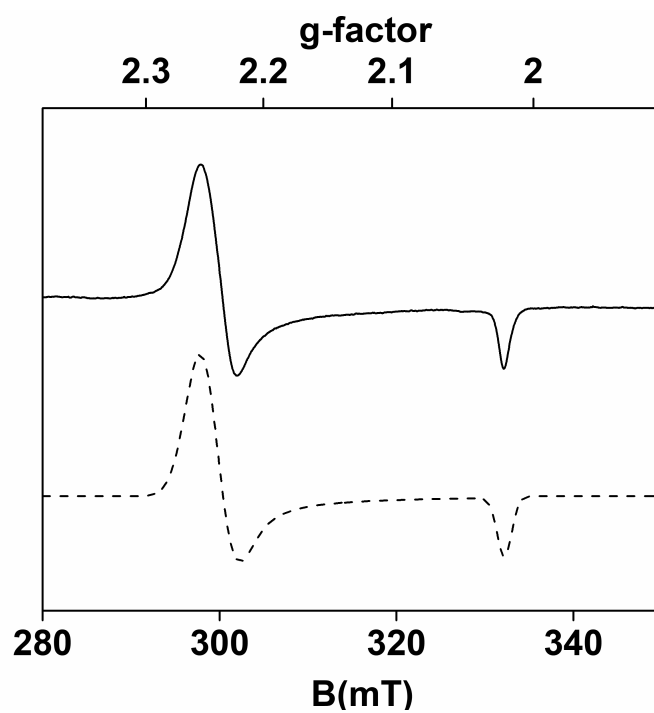


Figure A.25. Experimental (solid trace) and simulated (dashed trace) EPR spectra of **45b**.

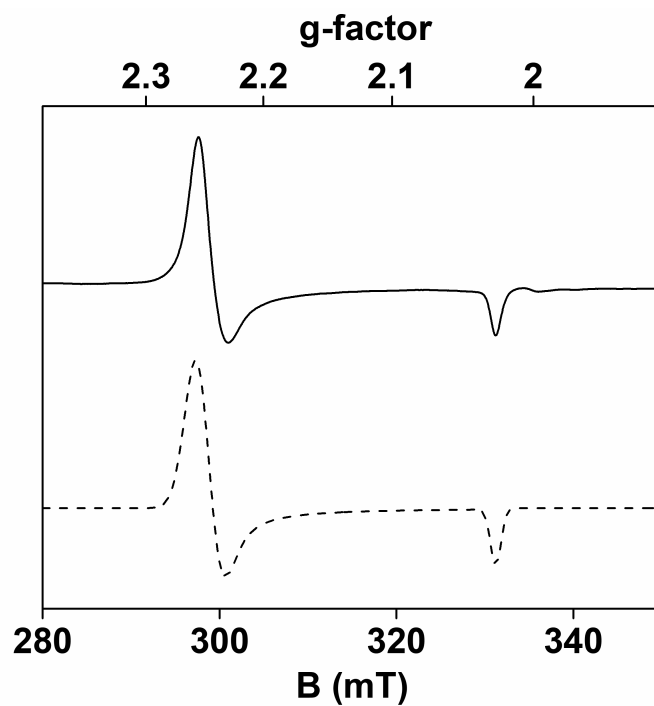


Figure A.26. Experimental (solid trace) and simulated (dashed trace) EPR spectra of **46b**.

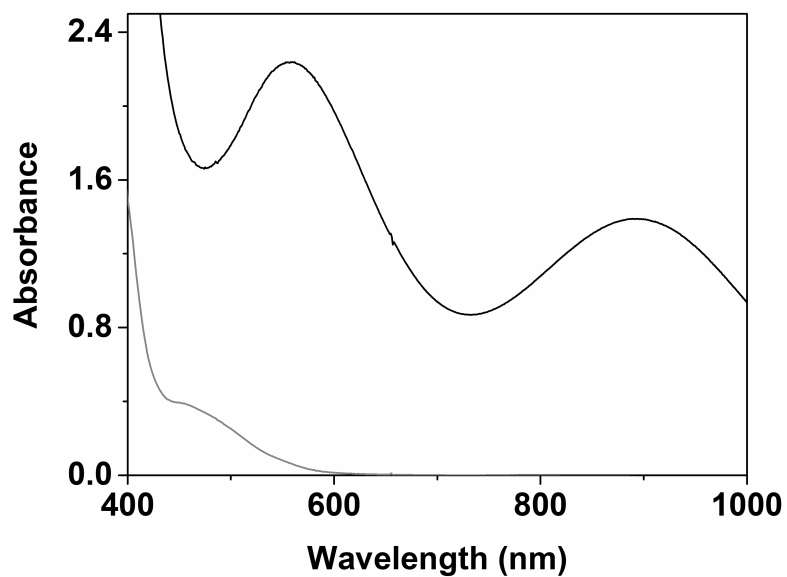


Figure A.27. Electronic absorption spectrum of **46a** (grey trace, 0.3 mM acetone solution, -40 °C) and of the oxidation product **46b** (black trace) obtained after the addition of methanolic CAN (5 equiv.).

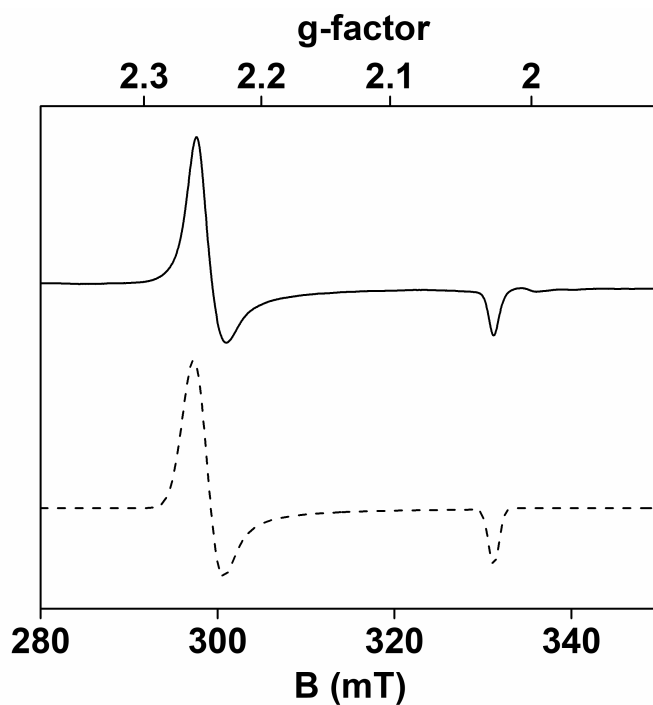


Figure A.28. EPR spectra of frozen solutions of **46b**, obtained by the oxidation of **46a** with CAN (5 equiv., top) or magic blue (1 equiv., bottom).

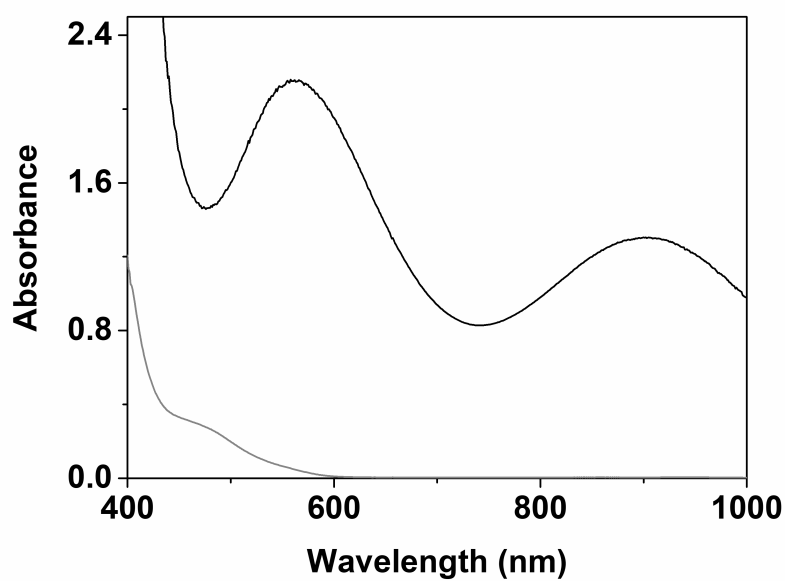


Figure A.29. Electronic absorption spectrum of **44a** (grey trace, 0.3 mM acetone solution, -40 °C) and of the oxidation product (**46b**, black trace) obtained after the addition of methanolic CAN (5 equiv.).

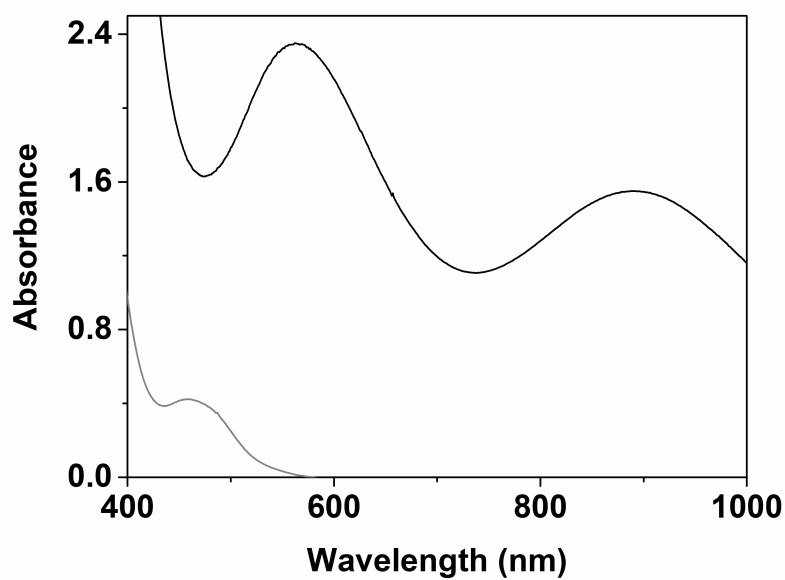


Figure A.30. Electronic absorption spectrum of **45a** (grey trace, 0.3 mM acetone solution, -40 °C) and of the oxidation product (**46b**, black trace) obtained after the addition of methanolic CAN (5 equiv.).

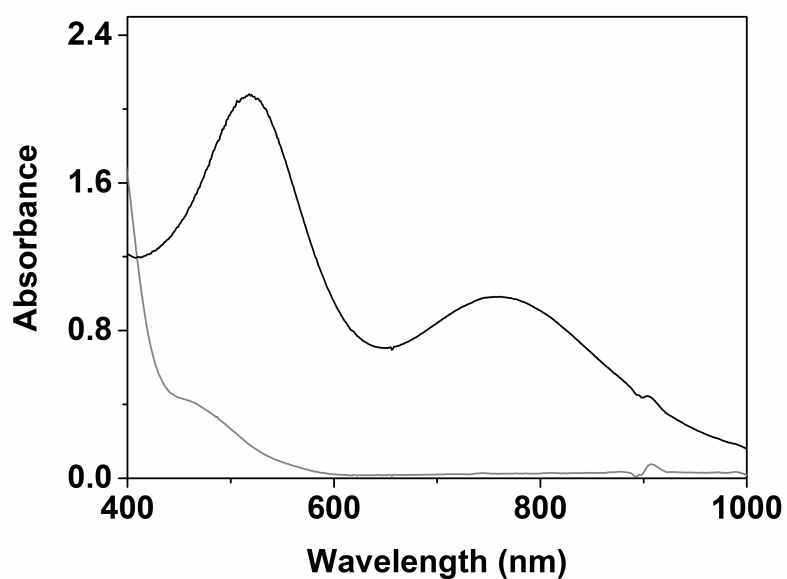


Figure A.31. Electronic absorption spectrum of **45a** (grey trace, 0.3 mM acetone solution, -40 °C) and of the oxidation product (**45b**, black trace) obtained after the addition of NaOCl/AcOH (15 equiv.).

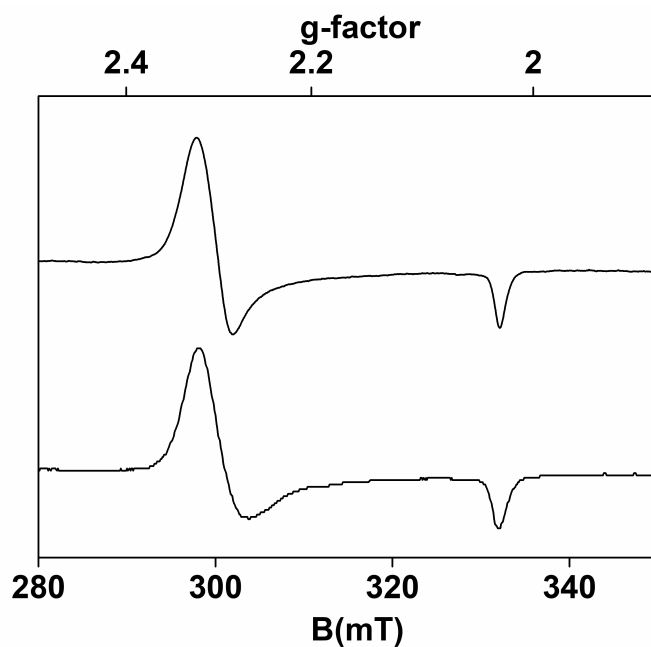


Figure A.32. EPR spectra of frozen solutions of **45b**, obtained by the oxidation of **45a** with magic blue (1 equiv., top), or NaOCl/AcOH (15 equiv., bottom).

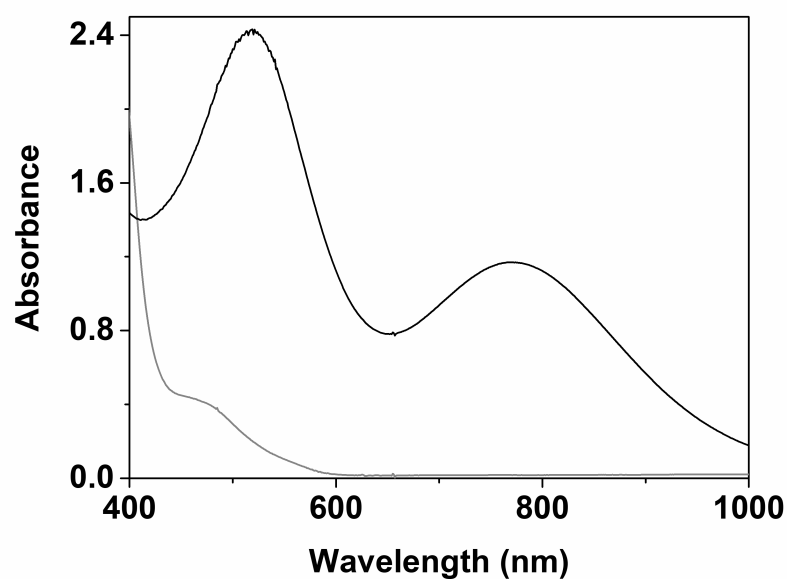


Figure A.33. Electronic absorption spectrum of **44a** (grey trace, 0.3 mM acetone solution, -40 °C) and of the oxidation product (**45b**, black trace) obtained after the addition of NaOCl/AcOH (15 equiv.).

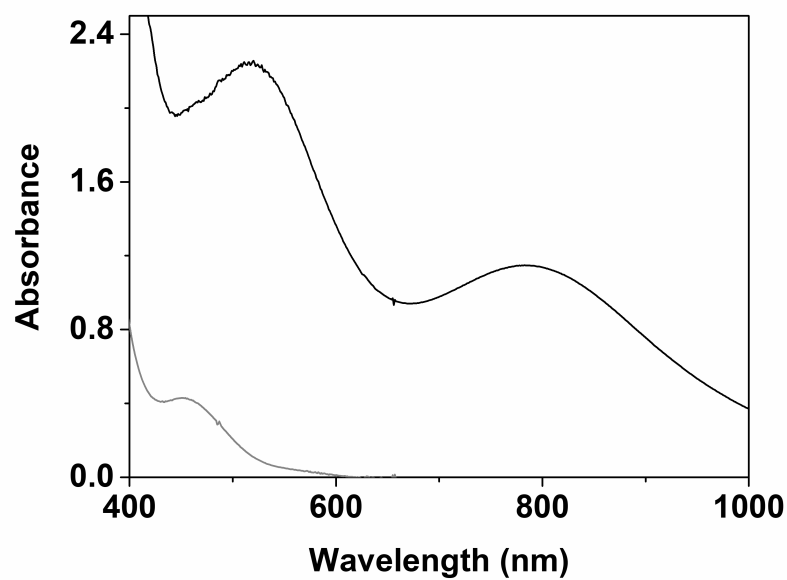


Figure A.34. Electronic absorption spectrum of **46a** (grey trace, 0.3 mM acetone solution, -40 °C) and of the oxidation product (**45b**, black trace) obtained after the addition of NaOCl/AcOH (15 equiv.).

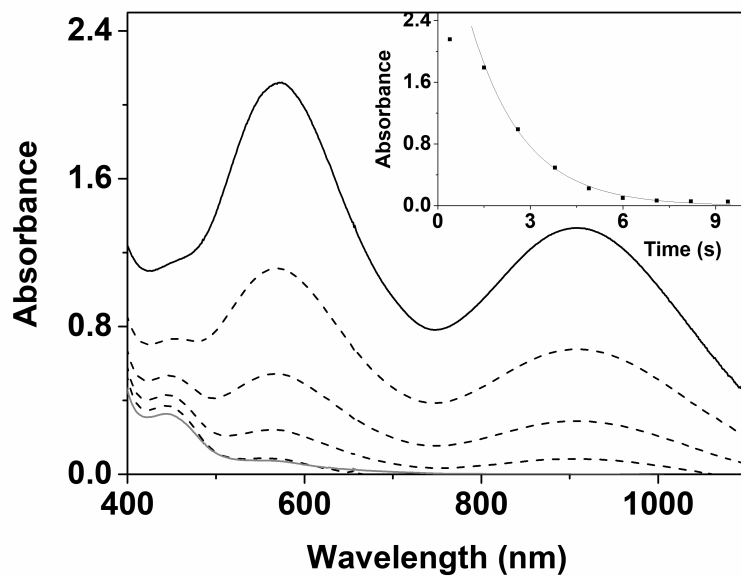


Figure A.35. Changes in the electronic absorption spectrum during the decay of **46b** in the presence of 10 equivalents of 2,4-DTPB, at -40 °C. Inset: time trace of the absorbance at 560 nm.

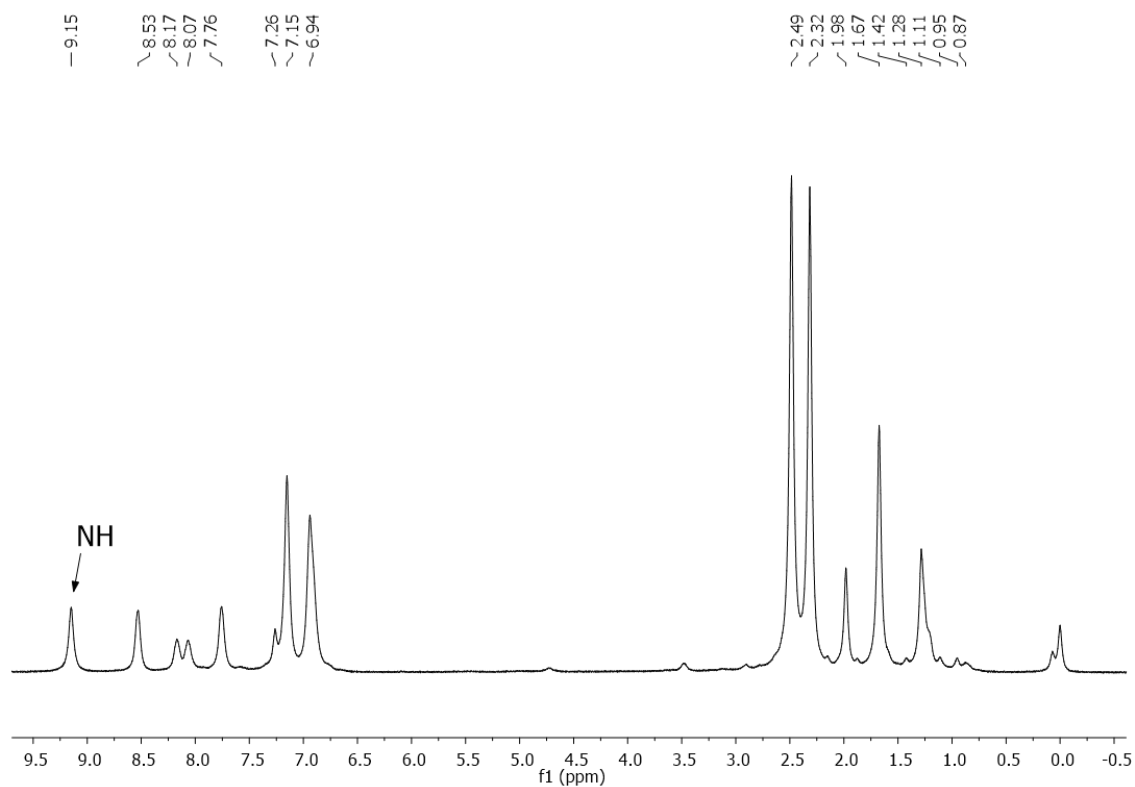


Figure A.36. ¹H NMR spectrum of a solution of **47** after the addition of 1 equivalent AcOH (400 MHz, CDCl₃) Line broadening is due to the precipitation of Ni salts.

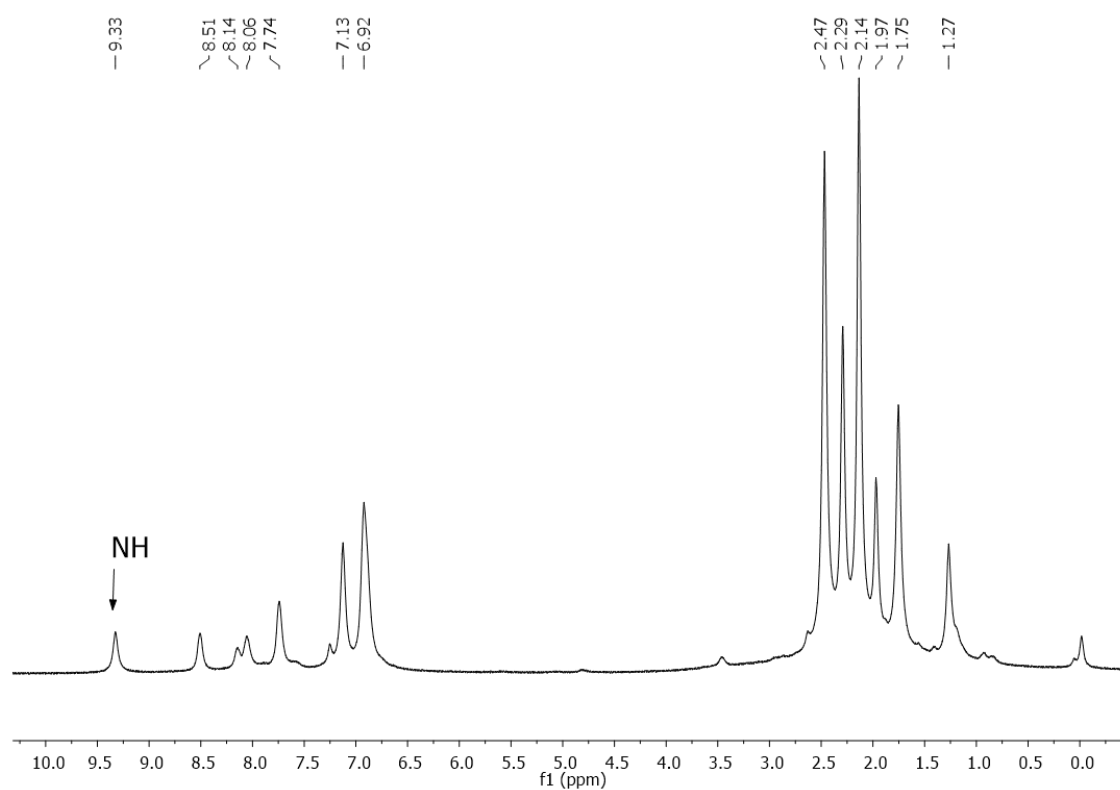


Figure A.37. ^1H NMR spectrum of a solution of **47** after the addition of 1 equivalent HNO_3 (400 MHz, CDCl_3) Line broadening is due to the precipitation of Ni salts.

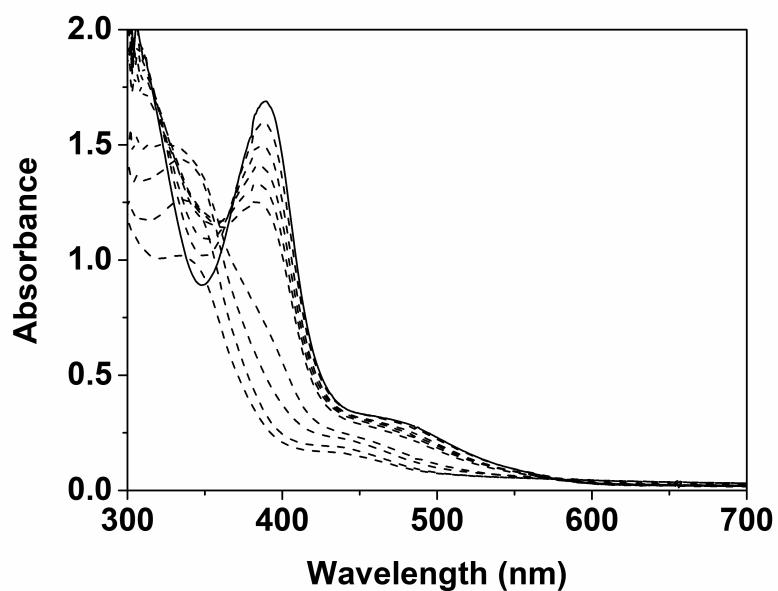


Figure A.38. Changes in the electronic absorption spectrum of **45a** (0.25 mM, black trace) on titration with $\text{Et}_2\text{O} \cdot \text{HBF}_4$ (up to 2 equiv.).

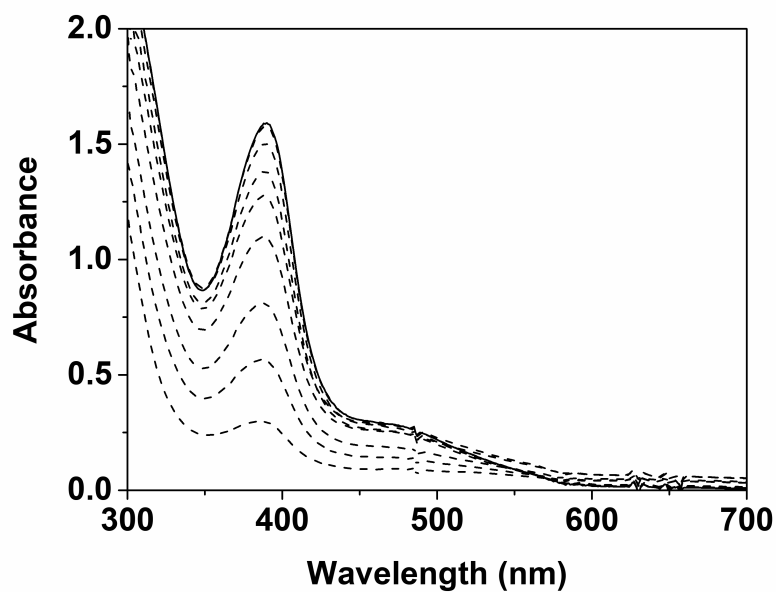


Figure A.39. Changes in the electronic absorption spectrum of **45a** (0.25 mM, black trace) on titration with AcOH (up to 3 equiv.).

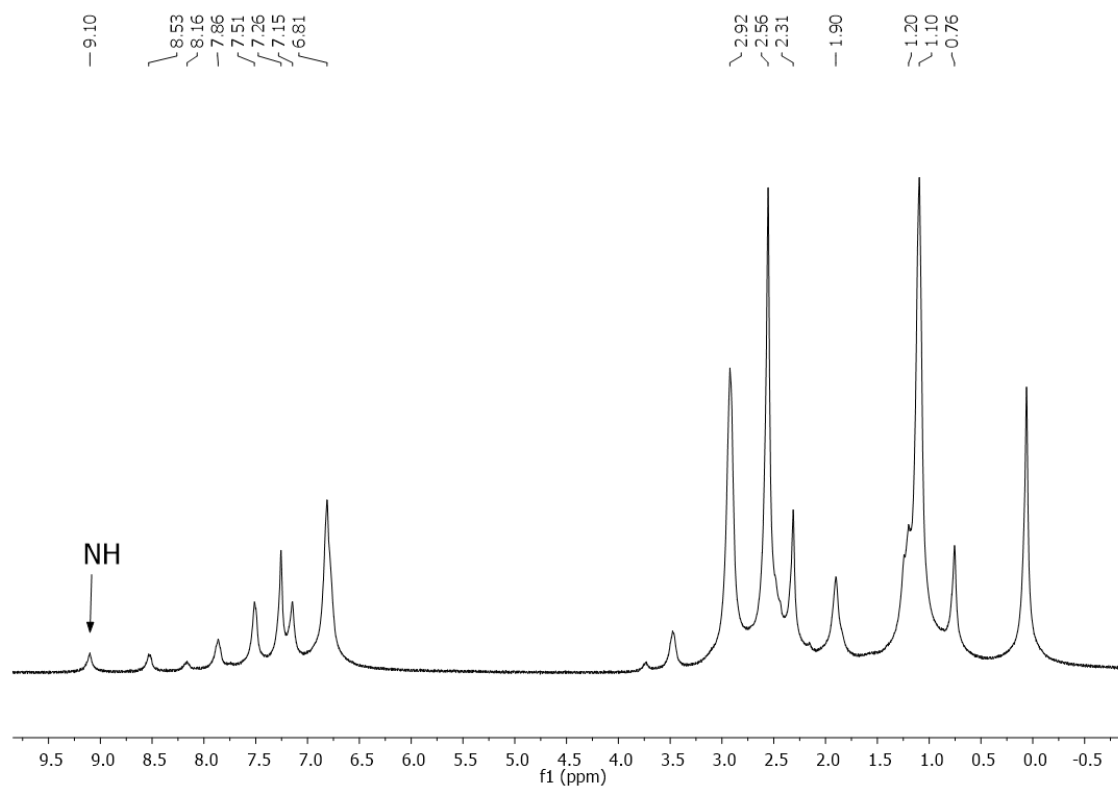


Figure A.40. ^1H NMR spectrum of a solution of **45a** after the addition of 1 equivalent $\text{Et}_2\text{O} \cdot \text{HBF}_4$ (400 MHz, CDCl_3). Line broadening is due to the precipitation of Ni salts.

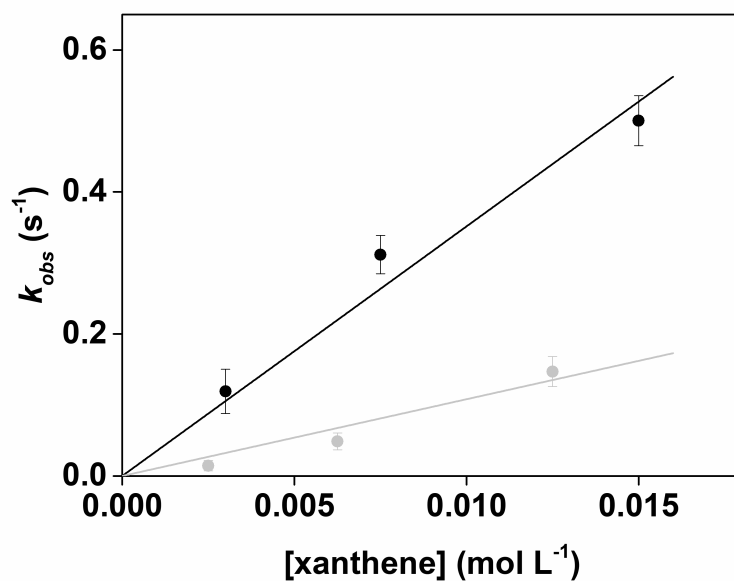


Figure A.41. Plots of k_{obs} versus [xanthene] determined for the reaction between **45b** and xanthene (black), and for the reaction between **45b** and [D₂]xanthene (grey), at 25 °C in acetone.

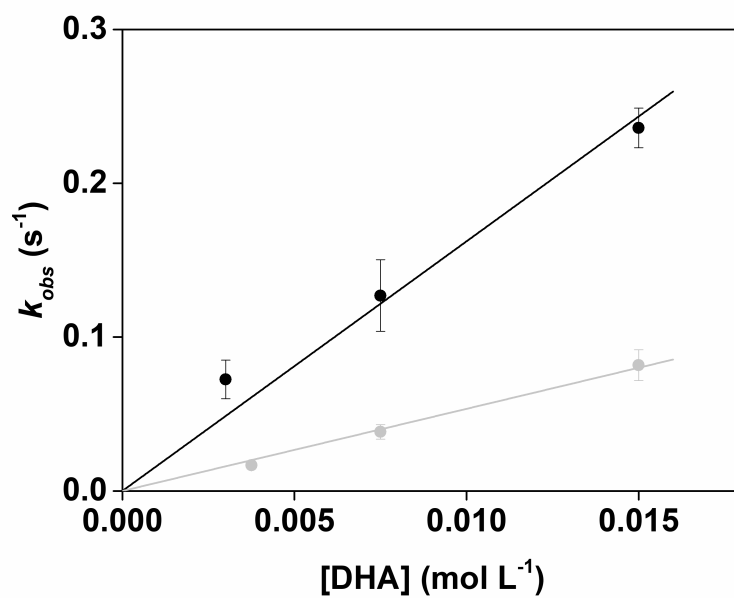


Figure A.42. Plots of k_{obs} versus [DHA] determined for the reaction between **45b** and DHA (black), and for the reaction between **45b** and [D₄]DHA (grey), at 25 °C in acetone.

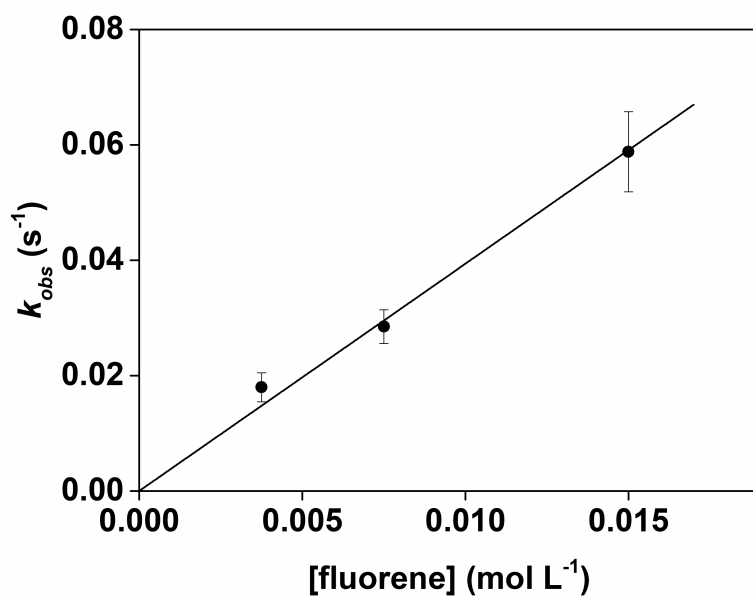


Figure A.43. Plot of k_{obs} versus [fluorene] determined for the reaction between **45b** and fluorene, at 25 °C in acetone.

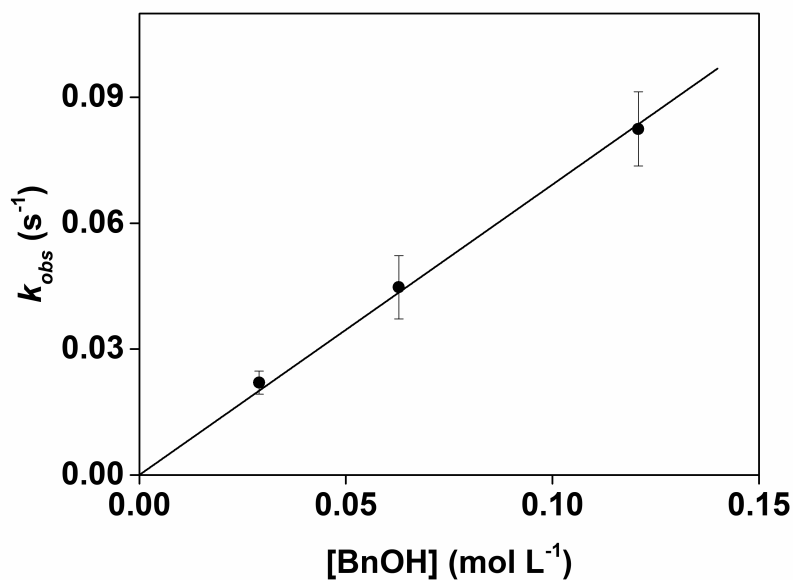


Figure A.44. Plot of k_{obs} versus [BnOH] determined for the reaction between **45b** and benzyl alcohol, at 25 °C in acetone.

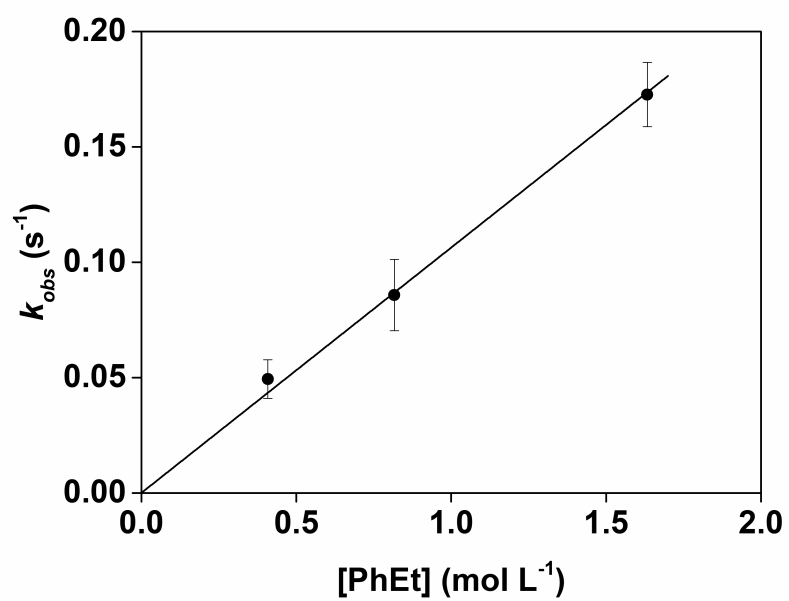


Figure A.45. Plot of k_{obs} versus $[PhEt]$ determined for the reaction between **45b** and ethylbenzene, at 25 °C in acetone.

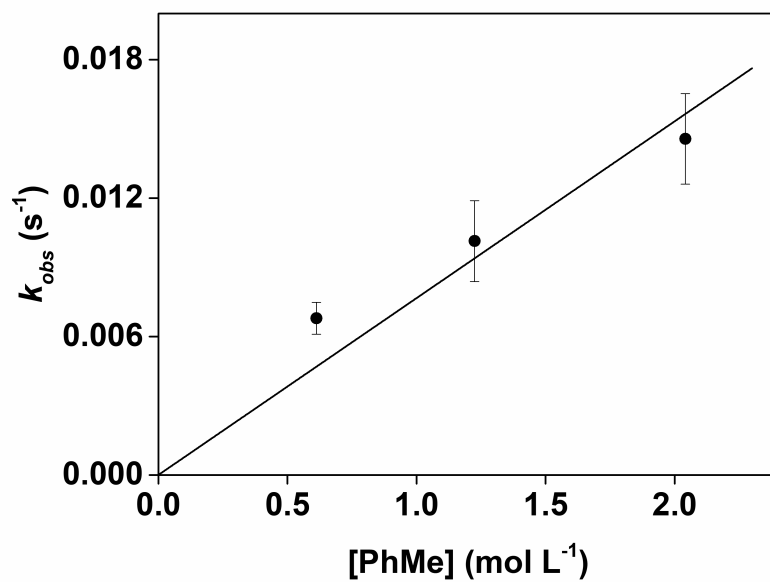


Figure A.46. Plot of k_{obs} versus $[PhMe]$ determined for the reaction between **45b** and toluene, at 25 °C in acetone.

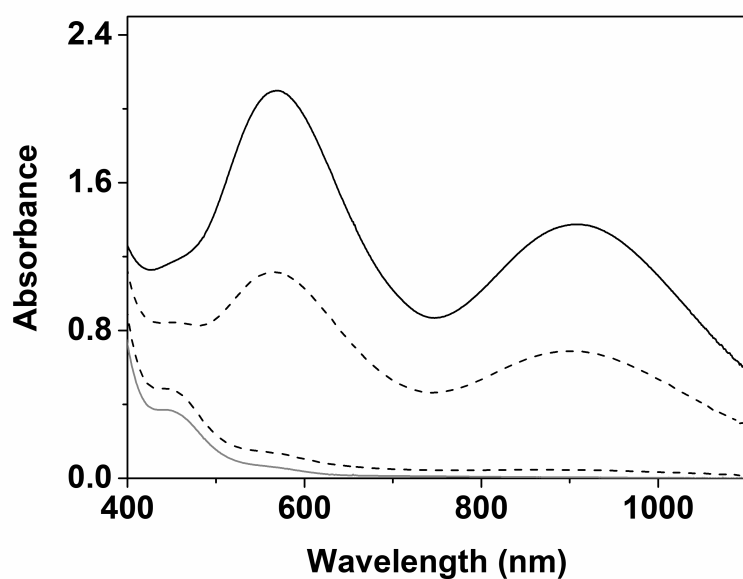


Figure A.47. Changes in the electronic absorption spectrum during the decay of **46b** in the presence of 5 equivalents of 10-methyl-9,10-dihydroacridine. The spectra were recorded at 0.5 s intervals.

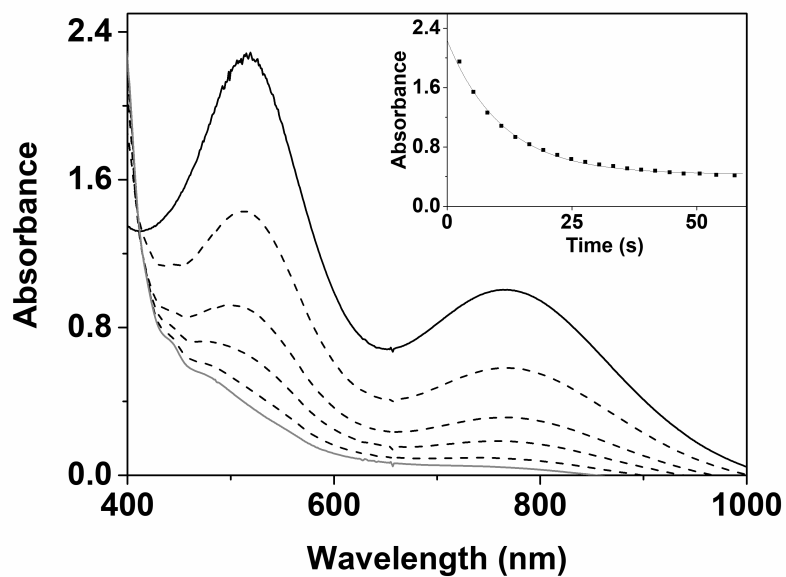


Figure A.48. Changes in the electronic absorption spectrum during the decay of **45b** in the presence of 50 equivalents of DHA. Inset: time trace of the absorbance at 510 nm.

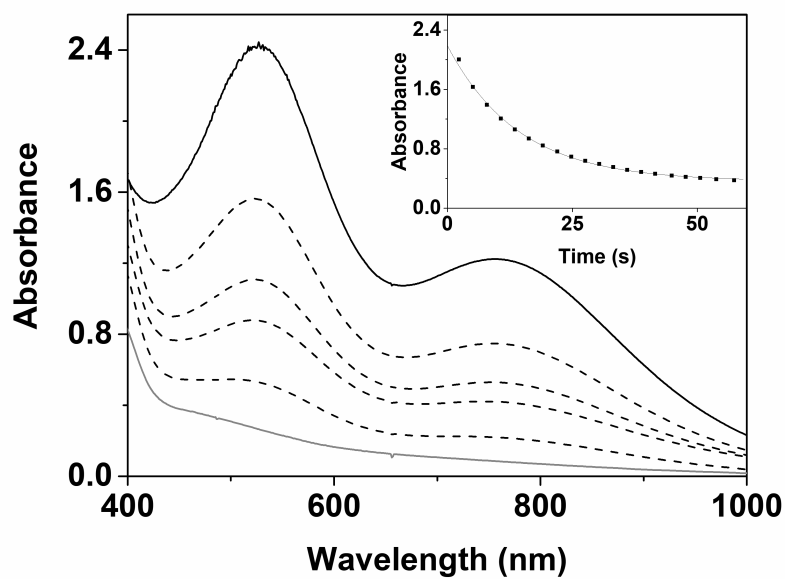


Figure A.49. Changes in the electronic absorption spectrum during the decay of **45b** in the presence of 210 equivalents of benzyl alcohol. Inset: time trace of the absorbance at 510 nm.

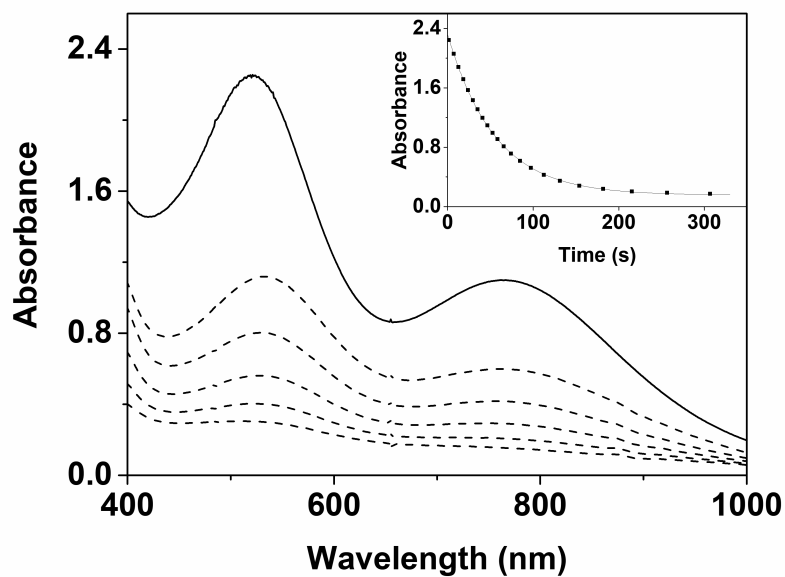


Figure A.50. Changes in the electronic absorption spectrum during the decay of **45b** in a 25/75 toluene/acetone mixture. Inset: time trace of the absorbance at 510 nm.

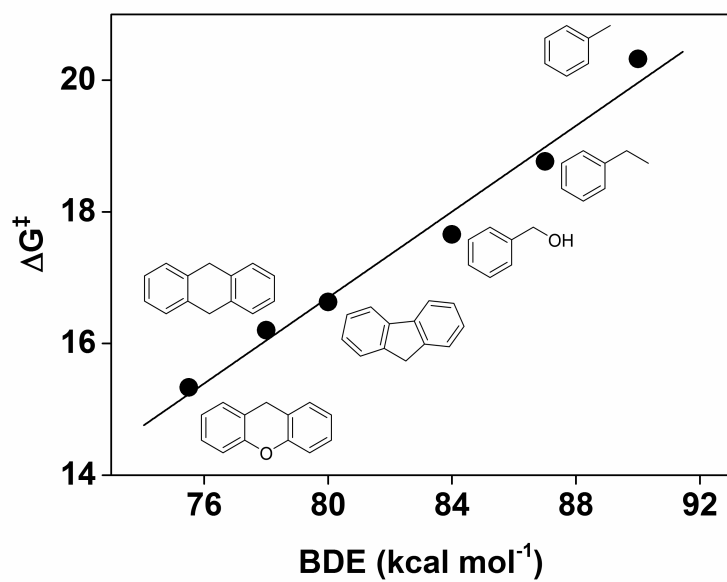
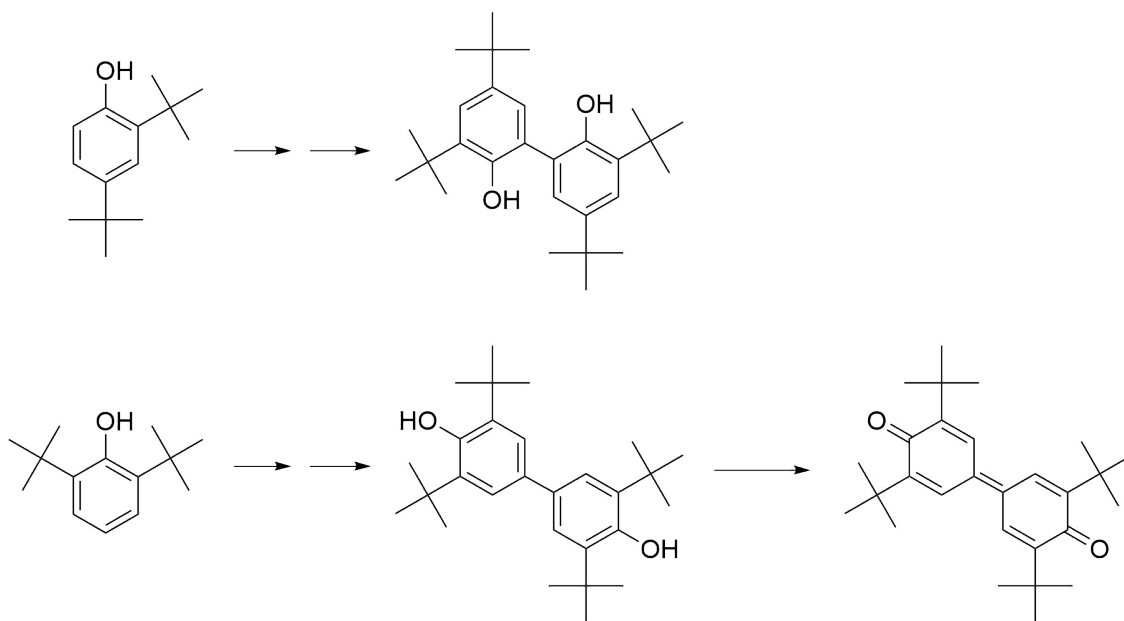
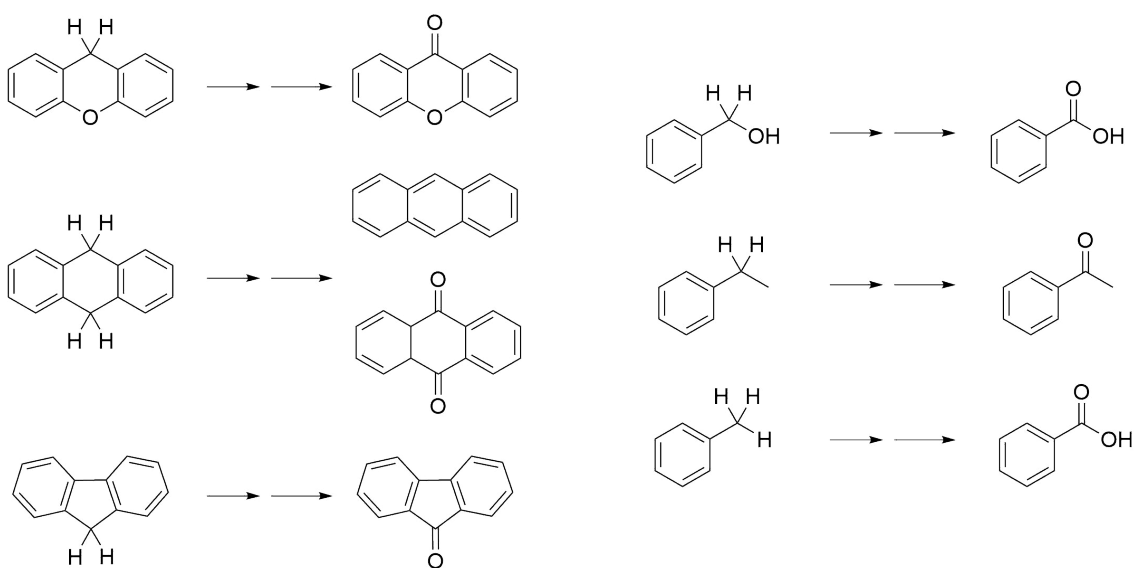


Figure A.51. Plot of $\Delta^\ddagger G$, for the reactions of **45b** with hydrocarbon substrates, measured at 25 °C, against the BDE_{C-H} of the substrates. $\Delta^\ddagger G$ was determined from k_2 via the Eyring equation.



Scheme A.1. Products identified in the oxidation of phenols by **45b** and **46b**.



Scheme A.2. Products identified in the oxidation of hydrocarbons by **45b**.

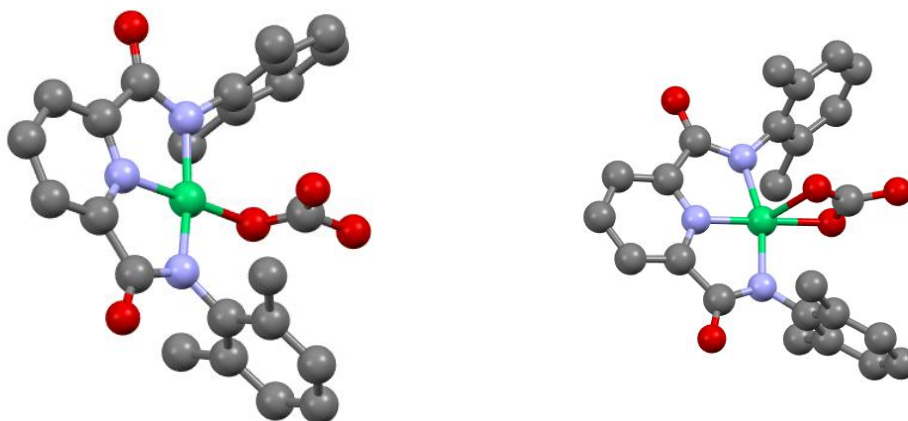


Figure A.52. DFT optimised structure of **44b** with unpaired electron in d_{xz} (left) and d_{z^2} (right).

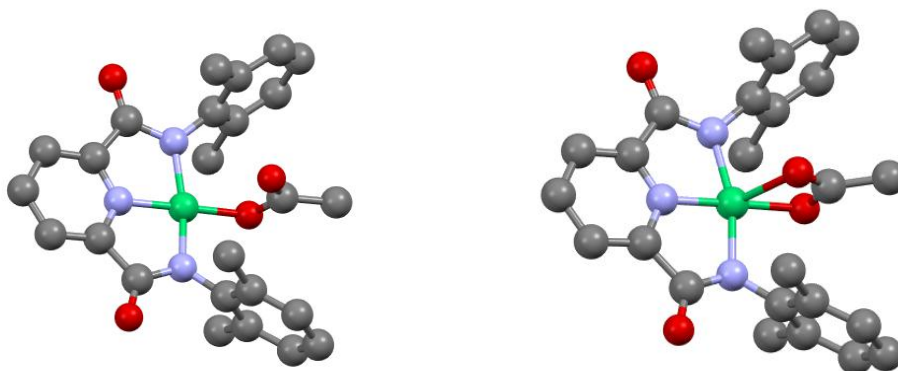


Figure A.53. DFT optimised structure of **45b** with unpaired electron in d_{xz} (left) and d_{z^2} (right).

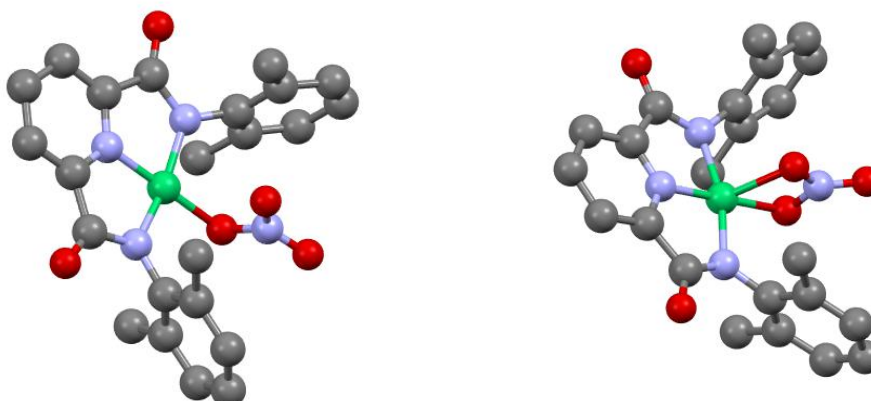


Figure A.54. DFT optimised structure of **46b** with unpaired electron in d_{xz} (left) and d_{z^2} (right).

A.3 Chapter 4

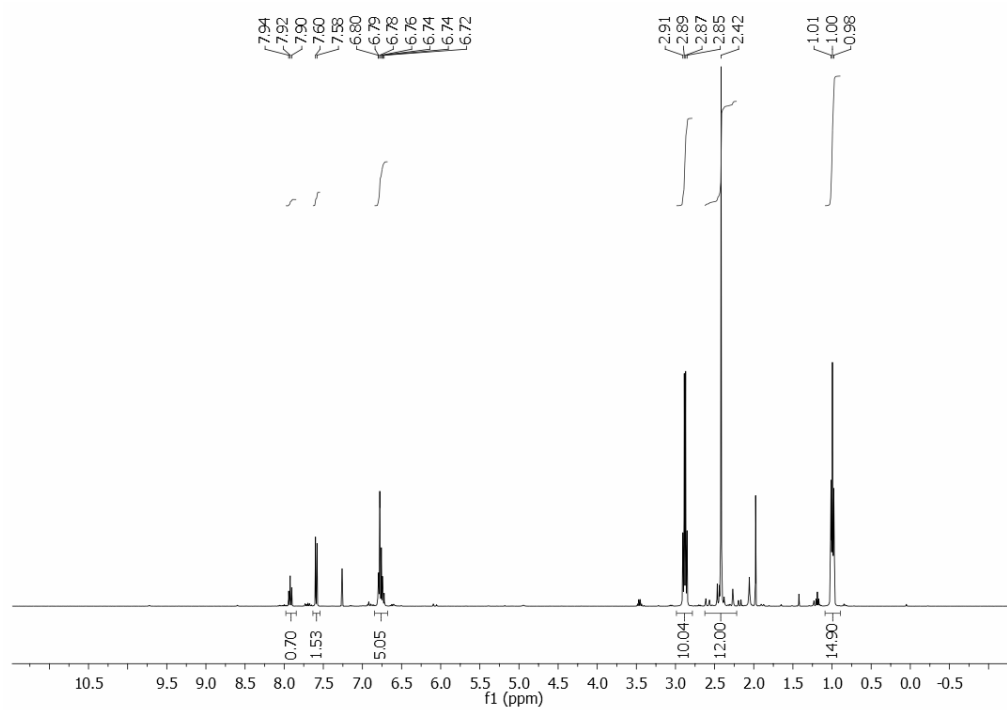


Figure A.55. ¹H NMR spectrum of **48a** (400 MHz, CDCl₃).

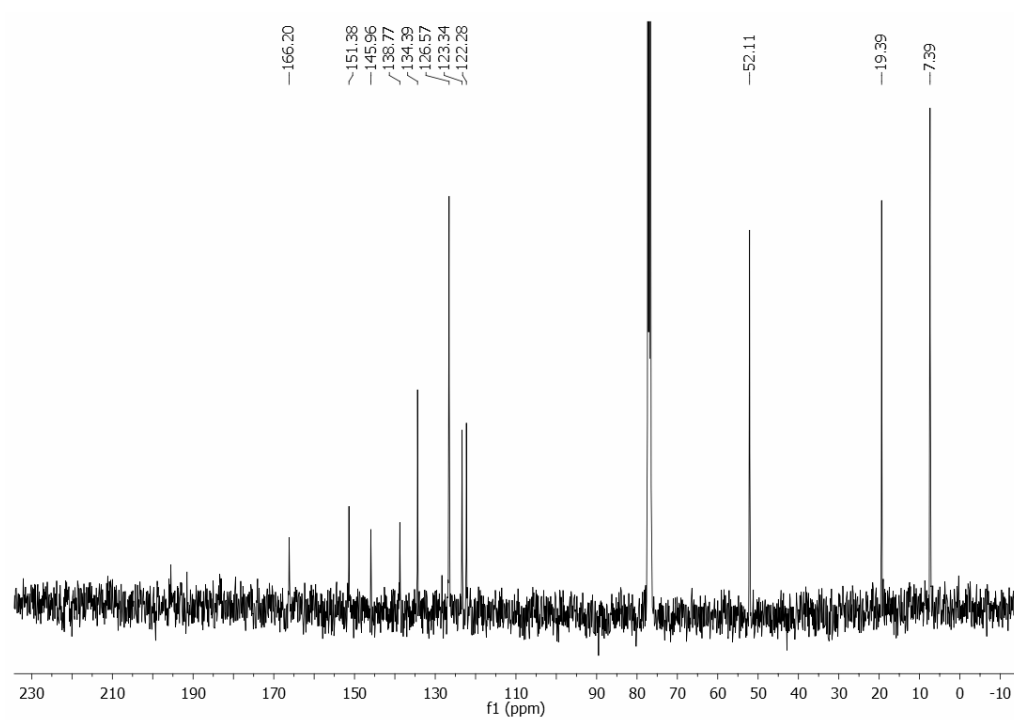


Figure A.56. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **48a** (101 MHz, CDCl_3).

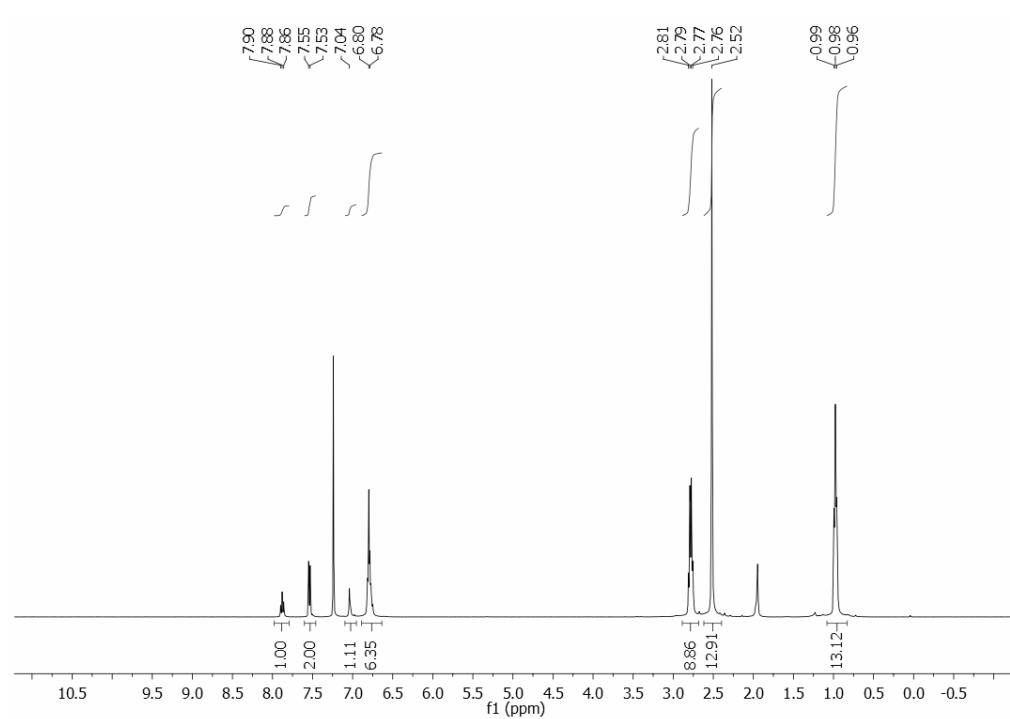


Figure A.57. ^1H NMR spectrum of **49a** (400 MHz, CDCl_3).

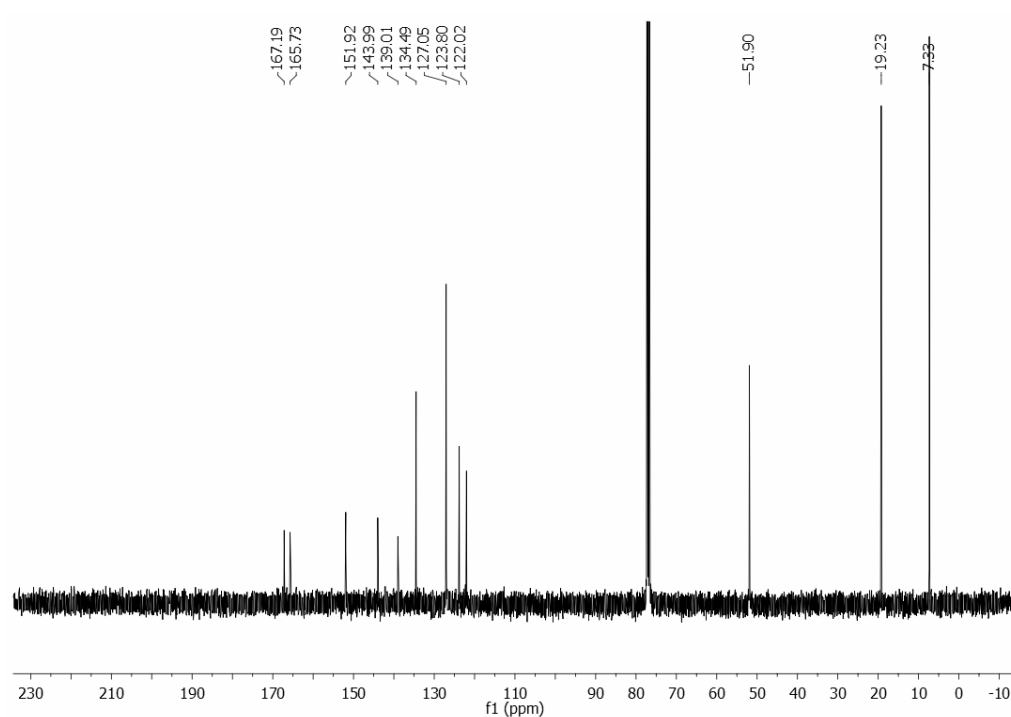


Figure A.58. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **49a** (101 MHz, CDCl_3).

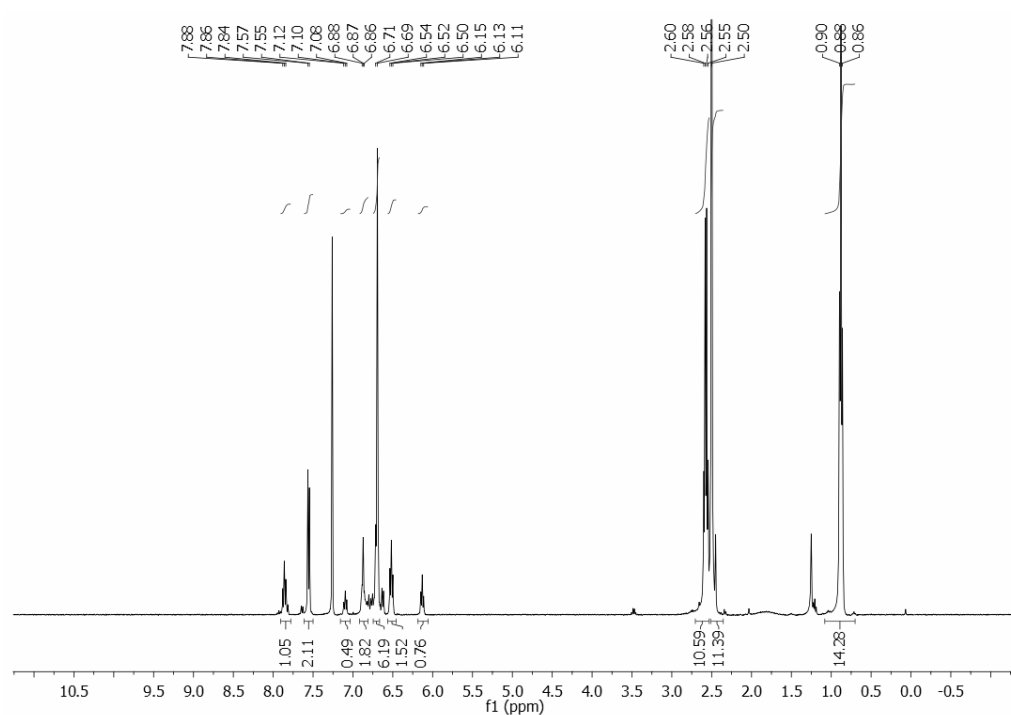


Figure A.59. ^1H NMR spectrum of **50a** (400 MHz, CDCl_3).

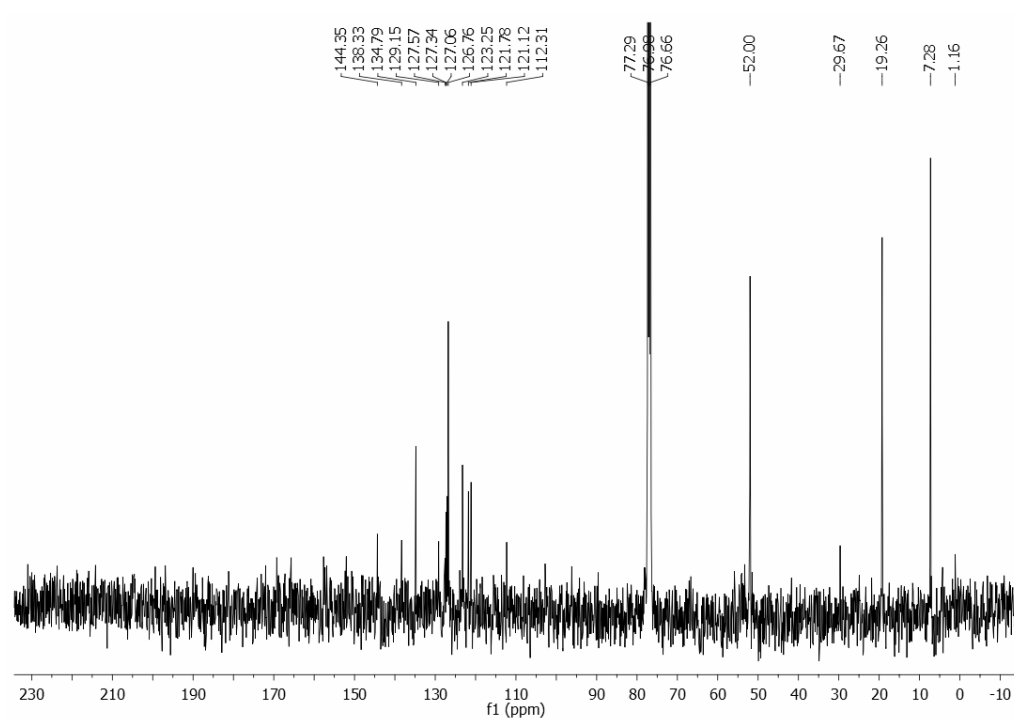


Figure A.60. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **50a** (101 MHz, CDCl_3).

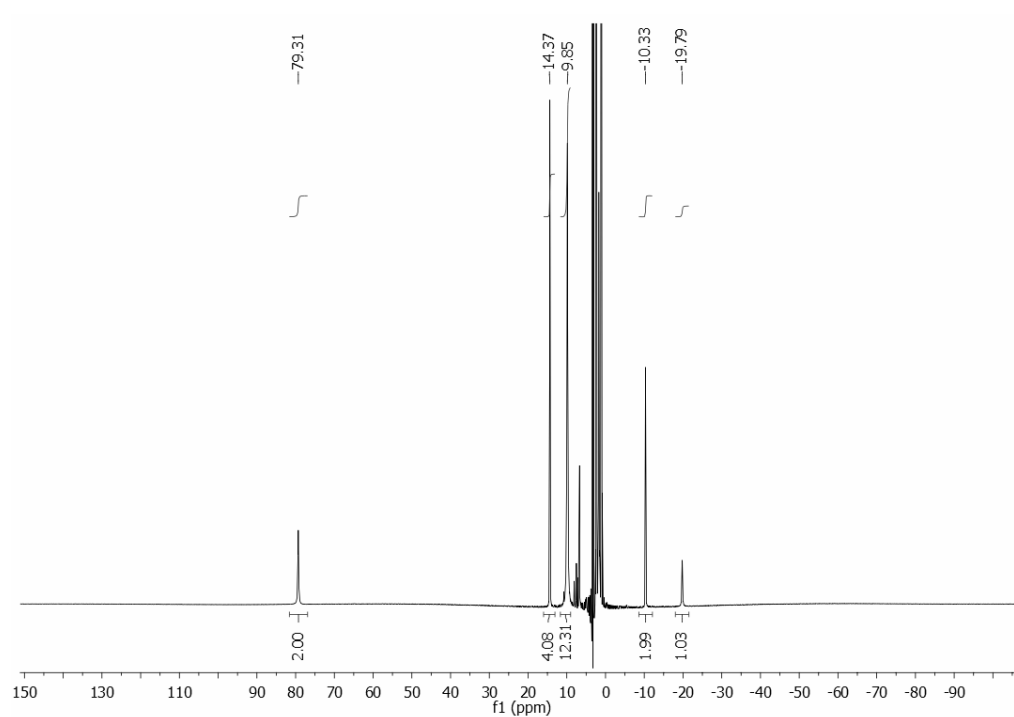


Figure A.61. ^1H NMR spectrum of **51a** (400 MHz, $[\text{D}_6]\text{DMSO}$).

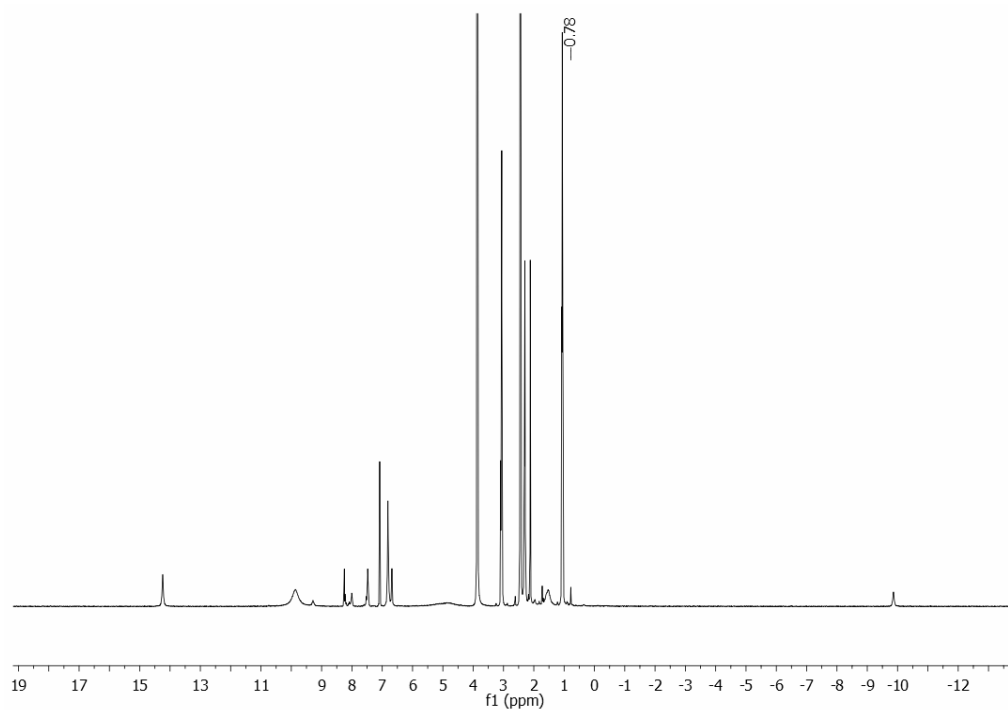


Figure A.62. ^1H NMR spectrum of **51a**, after 12 h from the addition of 0.1 mL D_2O (400 MHz, $[\text{D}_6]\text{DMSO}$). The peak at 0.78 ppm is indicative of formation of **45a**.

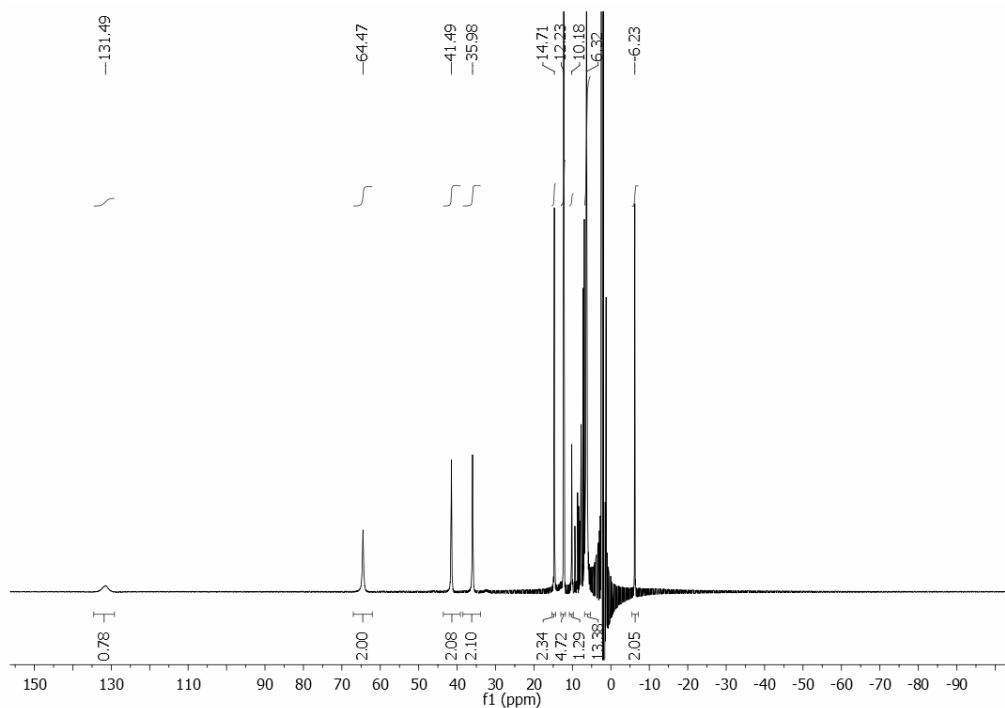


Figure A.63. ^1H NMR spectrum of **52a** (400 MHz, CD_3CN).

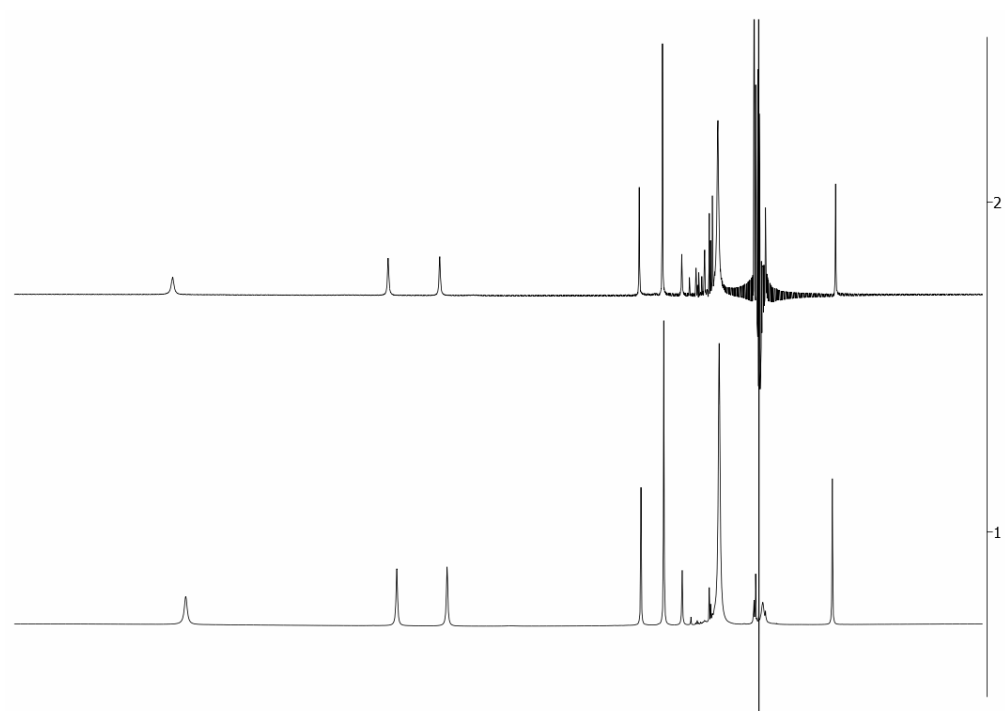


Figure A.64. Comparison of the ¹H NMR spectra of **52a** in CDCl₃ (top) and CD₃CN (bottom).

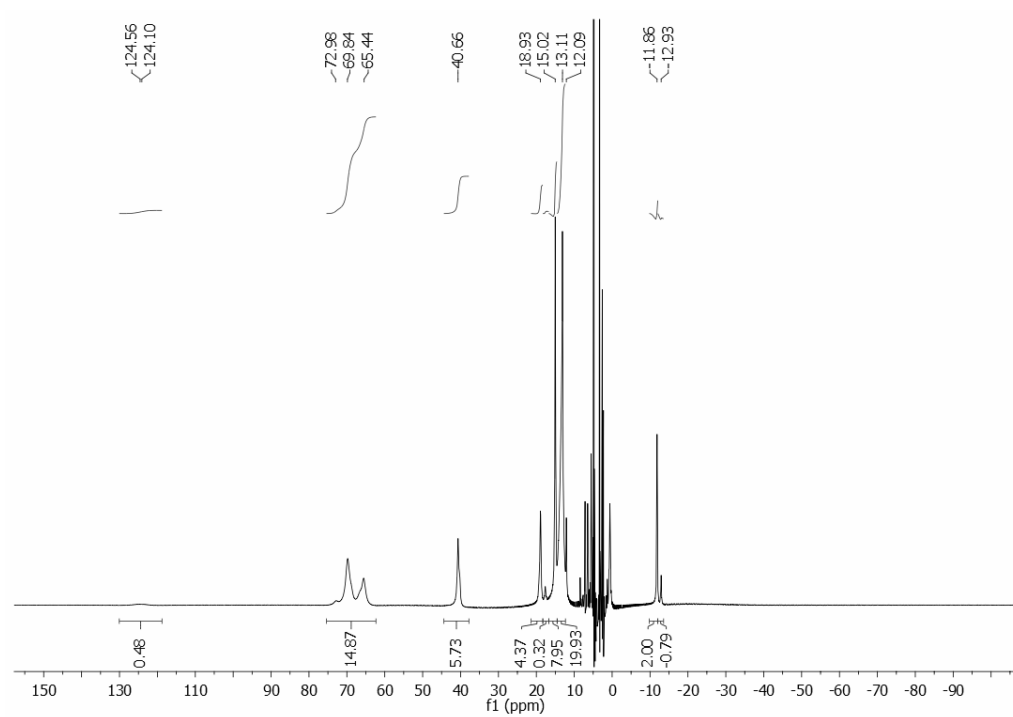


Figure A.65. ¹H NMR spectrum of **53a** (400 MHz, CD₃OD).

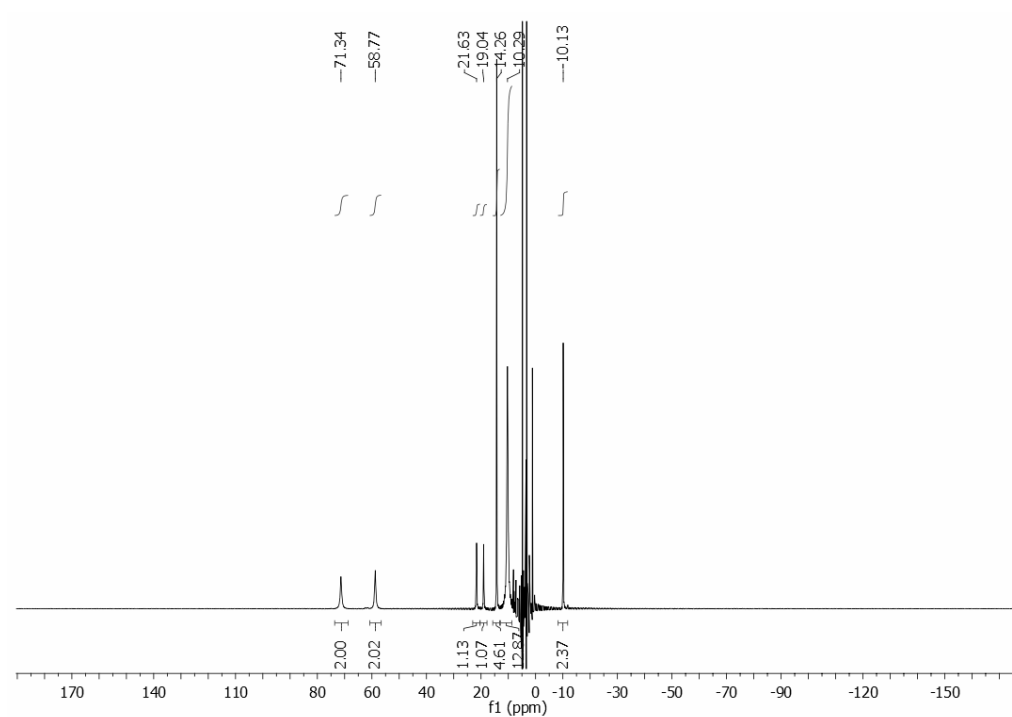


Figure A.66. ¹H NMR spectrum of **54a** (400 MHz, [D₆]DMSO).

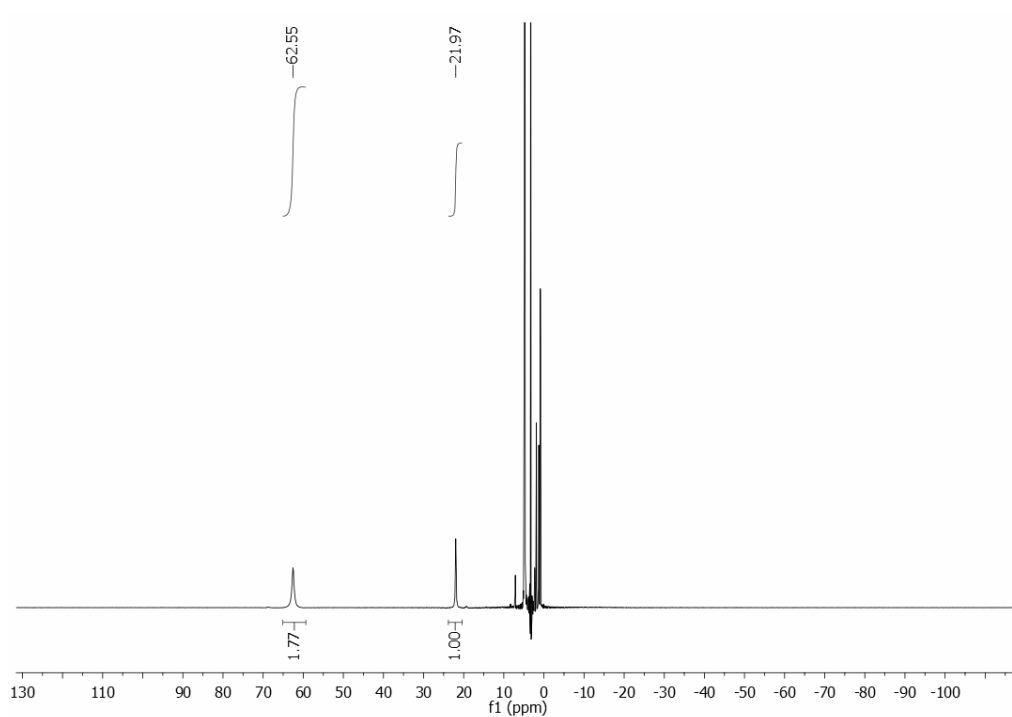


Figure A.67. ¹H NMR spectrum of **55** (400 MHz, [D₆]DMSO).

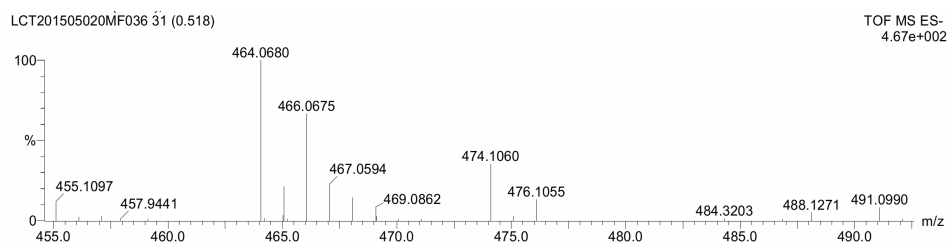


Figure A.68. Negative mode ESI MS spectrum of **48a**.

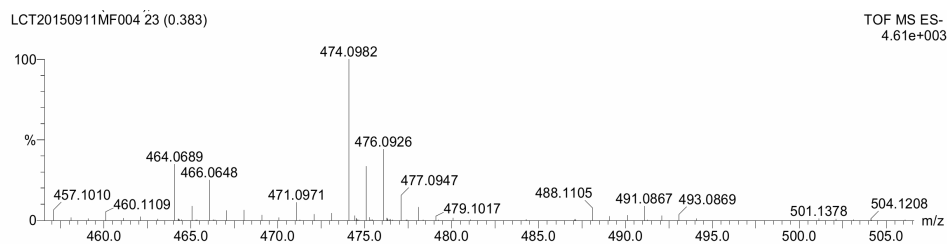


Figure A.69. Negative mode ESI MS spectrum of **49a**.

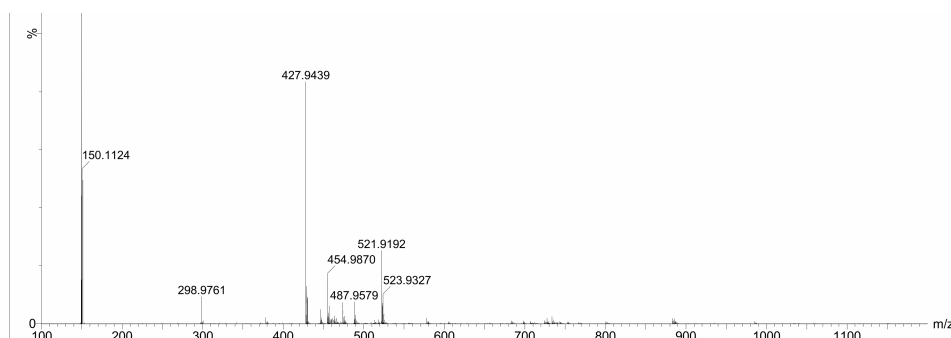


Figure A.70. Negative mode ESI MS spectrum of **50a**.

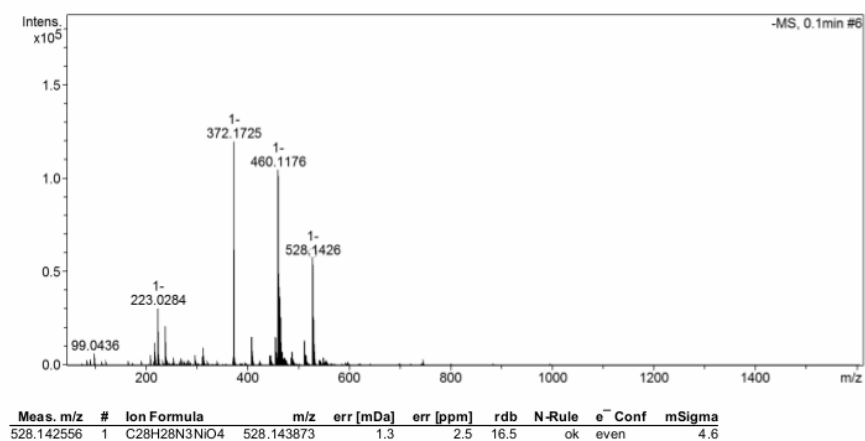


Figure A.71. Negative mode ESI MS spectrum of **51a**.

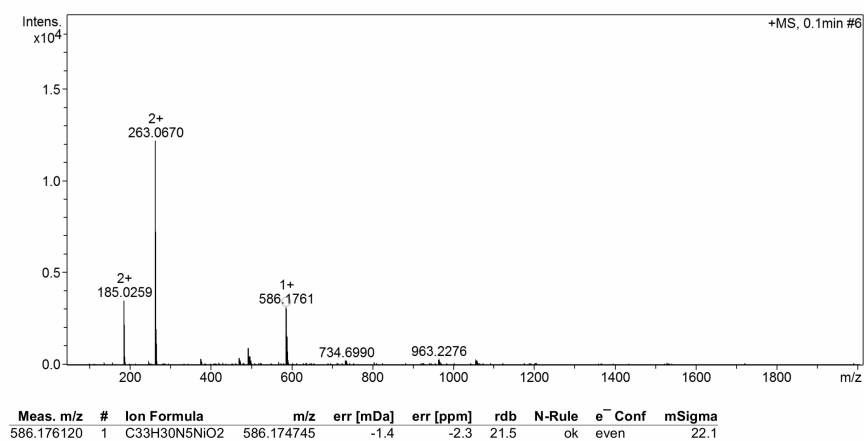


Figure A.72. Positive mode ESI MS spectrum of **52a**.

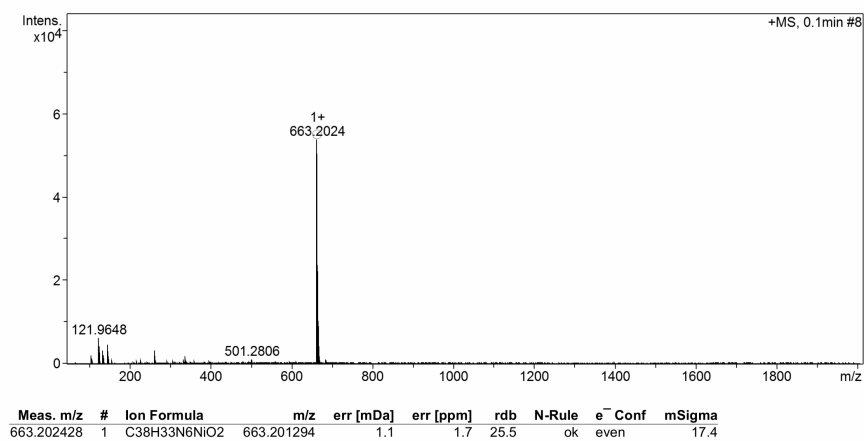


Figure A.73. Positive mode ESI MS spectrum of **53a**.

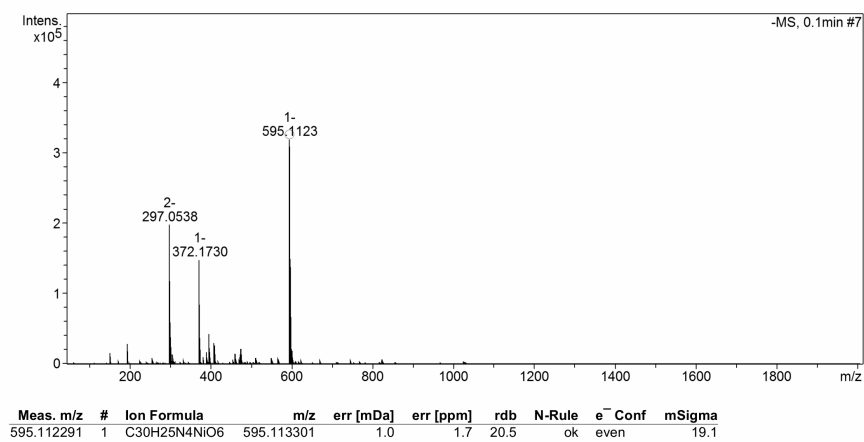


Figure A.74. Positive mode ESI MS spectrum of **54a**.

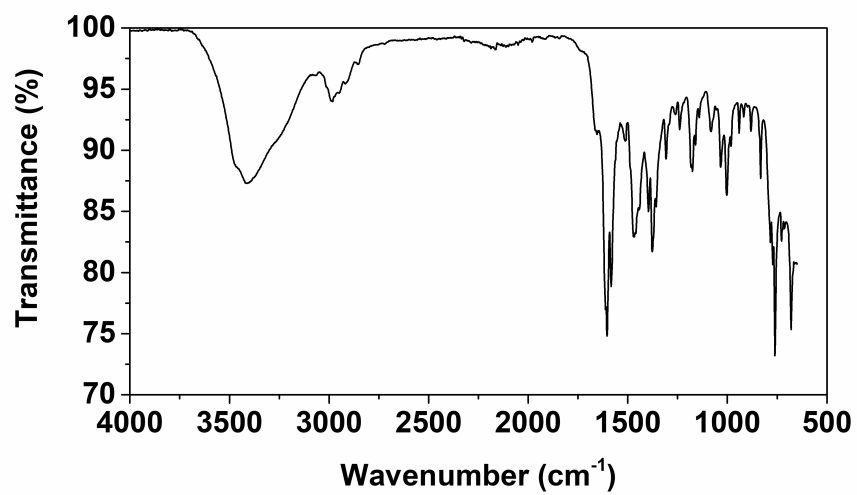


Figure A.75. ATR-FTIR spectrum of 48a.

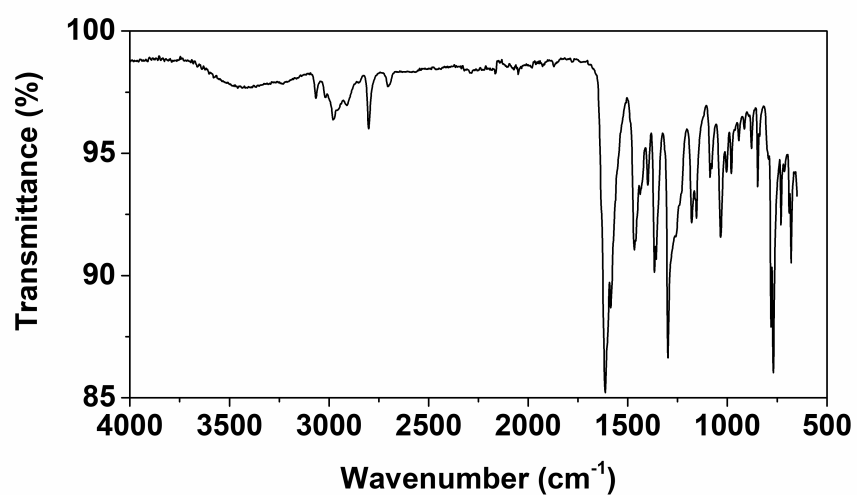


Figure A.76. ATR-FTIR spectrum of 49a.

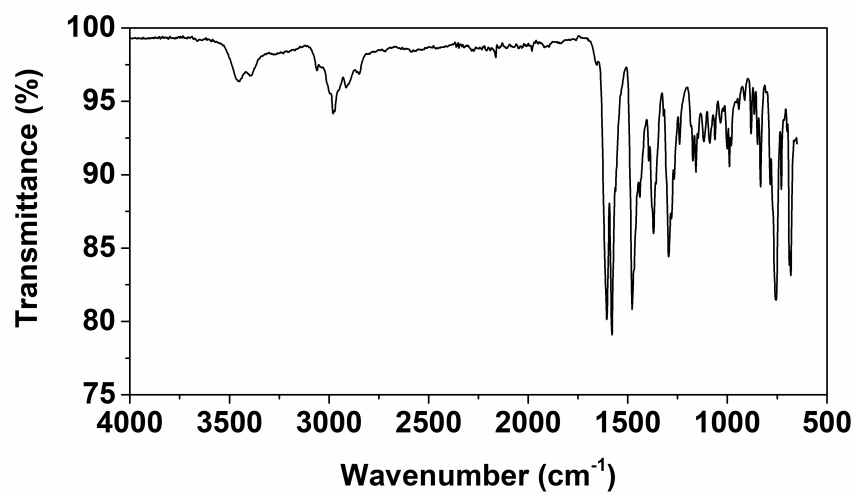


Figure A.77. ATR-FTIR spectrum of **50a**.

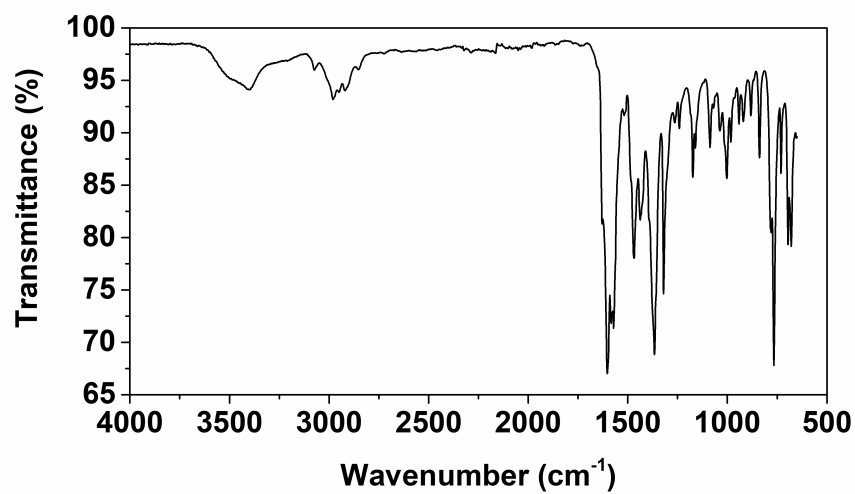


Figure A.78. ATR-FTIR spectrum of **51a**.

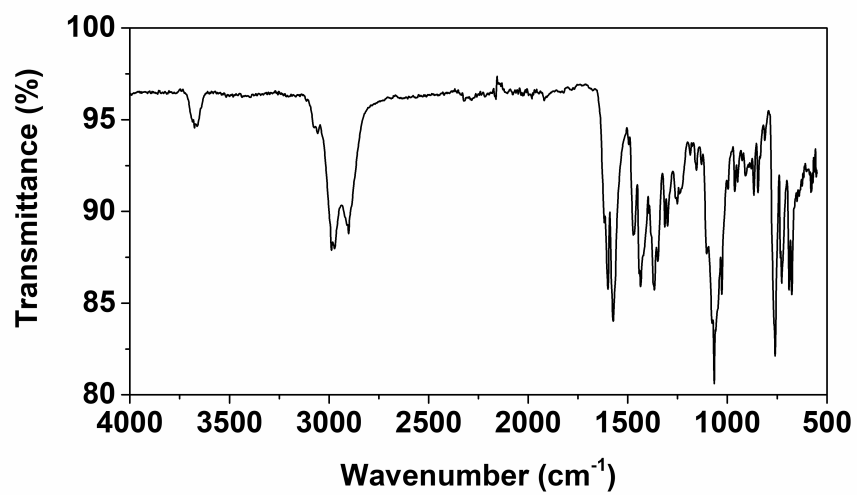


Figure A.79. ATR-FTIR spectrum of 52a.

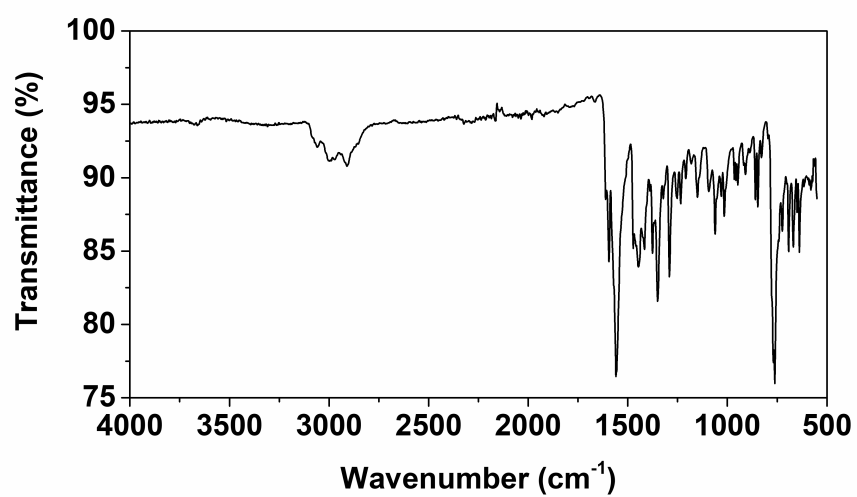


Figure A.80. ATR-FTIR spectrum of 53a.

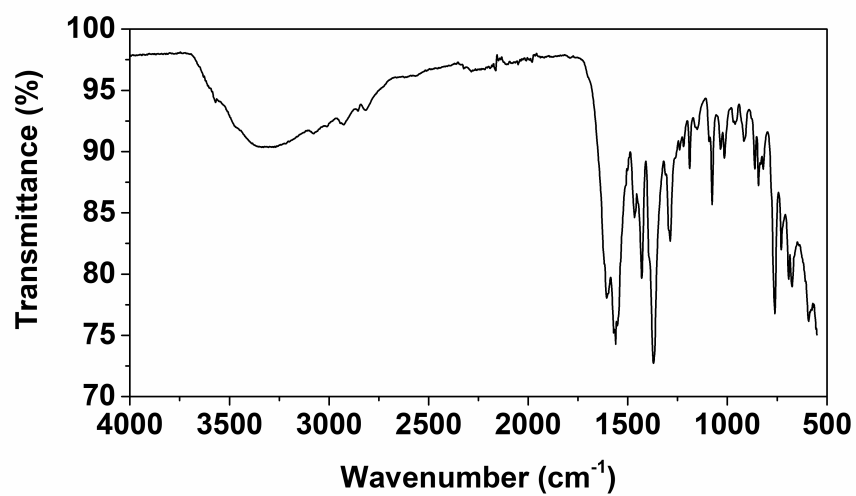


Figure A.81. ATR-FTIR spectrum of **54a**.

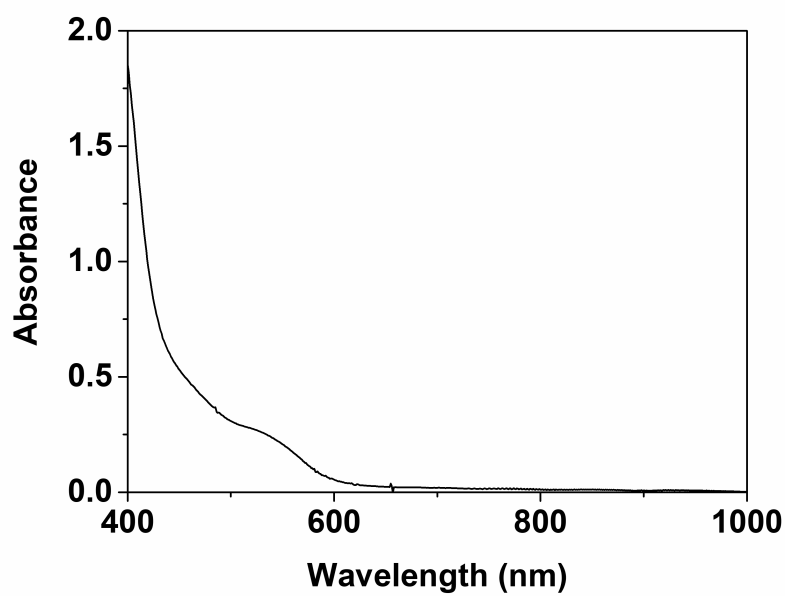


Figure A.82. UV-Vis spectrum of **50a** (acetone, 25 °C).

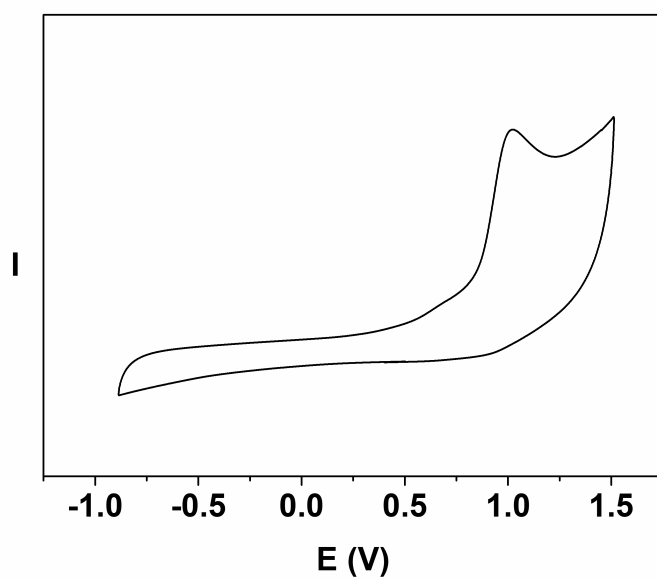


Figure A.83. Cyclic voltammogram of **47**, vs Fc^+/Fc (acetone, 25 °C, 0.1 M Bu_4NPF_6 , scan rate 0.05 V s^{-1}).

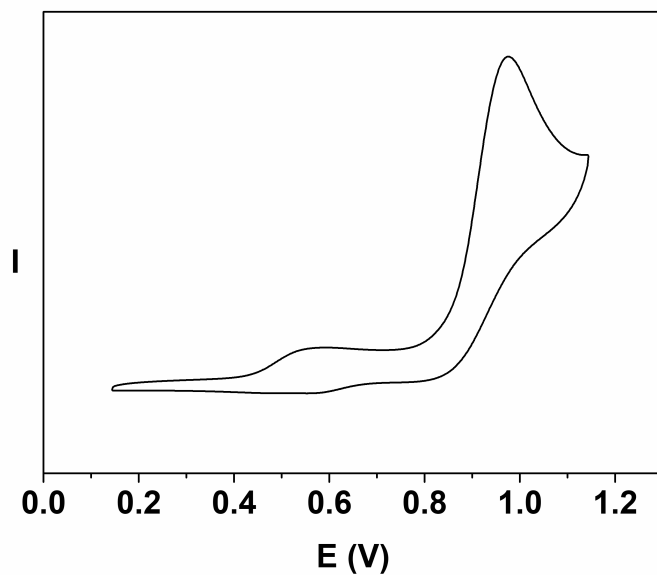


Figure A.84. Cyclic voltammogram of **49a**, vs Fc^+/Fc (acetone, 25 °C, 0.1 M Bu_4NPF_6 , scan rate 0.05 V s^{-1}).

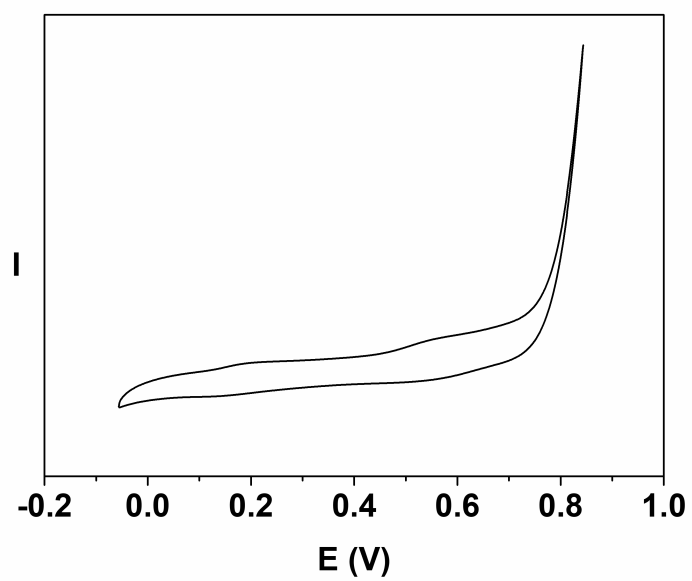


Figure A.85. Cyclic voltammogram of **50a**, vs Fc^+/Fc (acetone, 25 °C, 0.1 M Bu_4NPF_6 , scan rate 0.05 V s^{-1}).

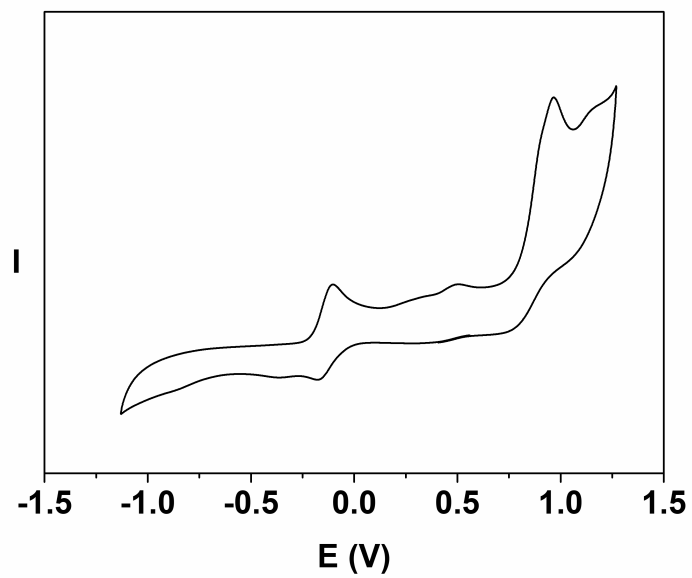


Figure A.86. Cyclic voltammogram of **51a**, vs Fc^+/Fc (acetone, 25 °C, 0.1 M Bu_4NPF_6 , scan rate 0.05 V s^{-1}).

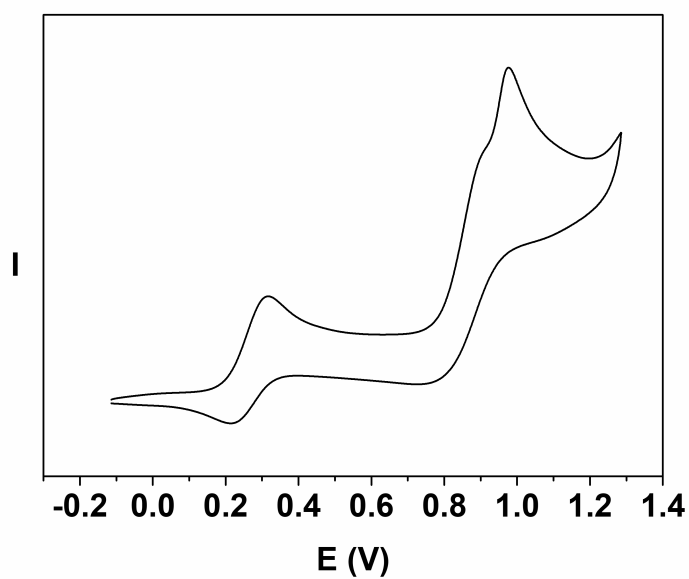


Figure A.87. Cyclic voltammogram of **52a**, vs Fc^+/Fc (acetone, 25 °C, 0.1 M Bu_4NPF_6 , scan rate 0.05 V s^{-1}).

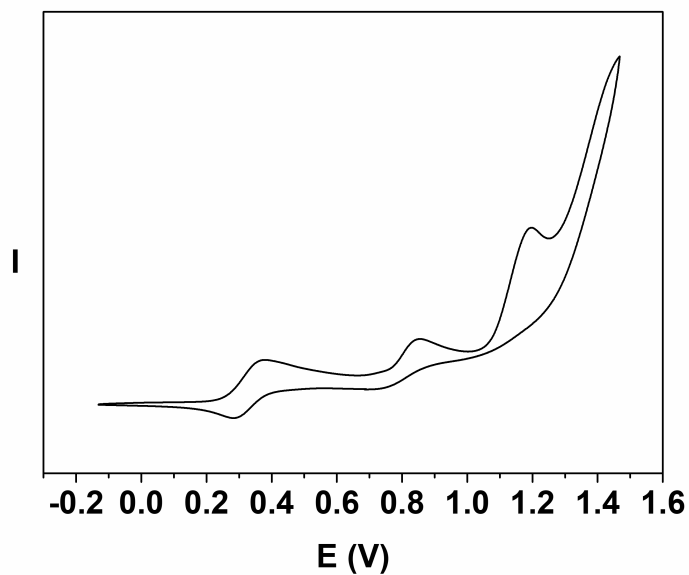


Figure A.88. Cyclic voltammogram of **53a**, vs Fc^+/Fc (acetone, 25 °C, 0.1 M Bu_4NPF_6 , scan rate 0.05 V s^{-1}).

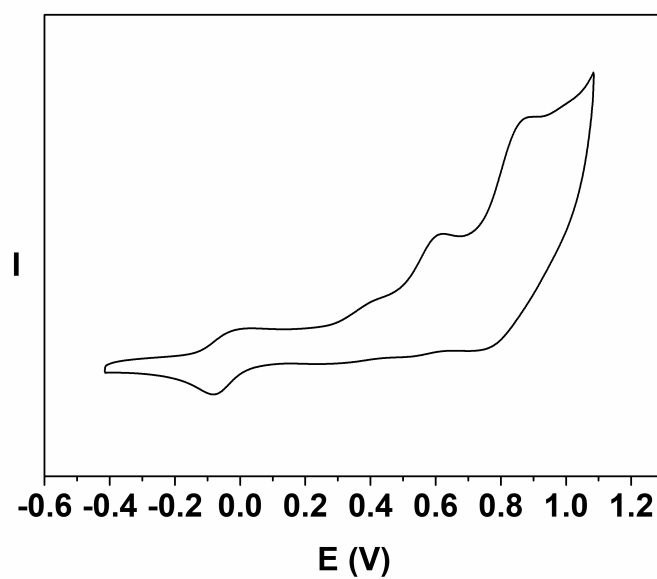


Figure A.89. Cyclic voltammogram of **54a**, vs Fc^+/Fc (acetone, 25 °C, 0.1 M Bu_4NPF_6 , scan rate 0.05 V s^{-1}).

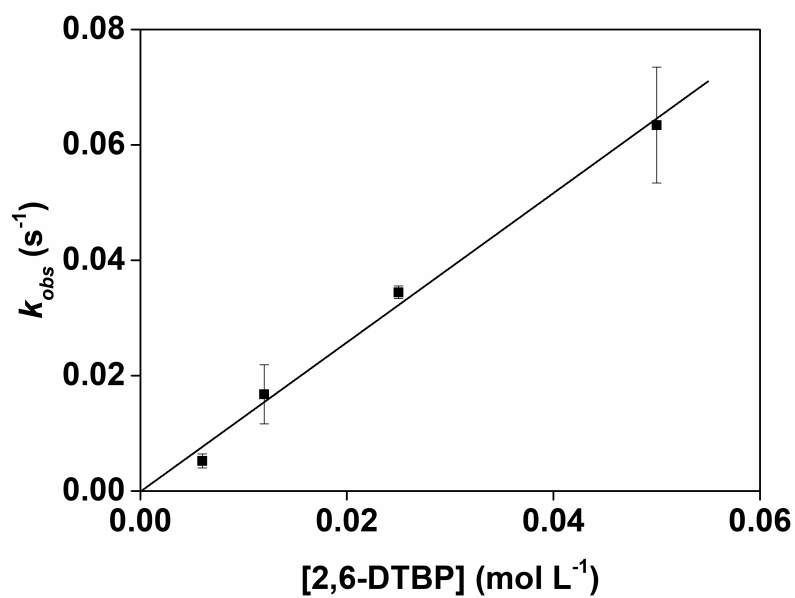


Figure A.90. Plot of k_{obs} versus [2,6-DTBP] determined for the reaction between **52b** and 2,6-DTBP, at -40 °C in acetone/acetonitrile 9/1.

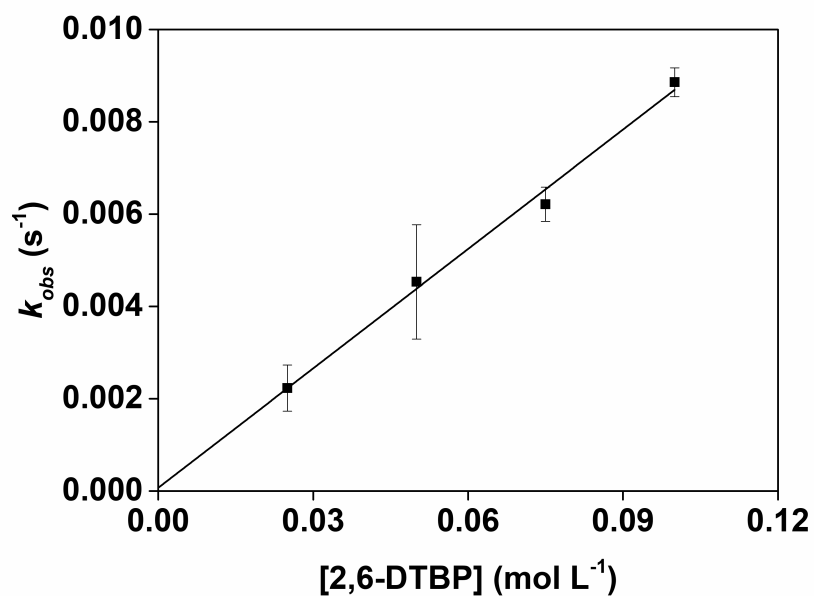


Figure A.91. Plot of k_{obs} versus [2,6-DTBP] determined for the reaction between **53b** and 2,6-DTBP, at -40 °C in methanol.

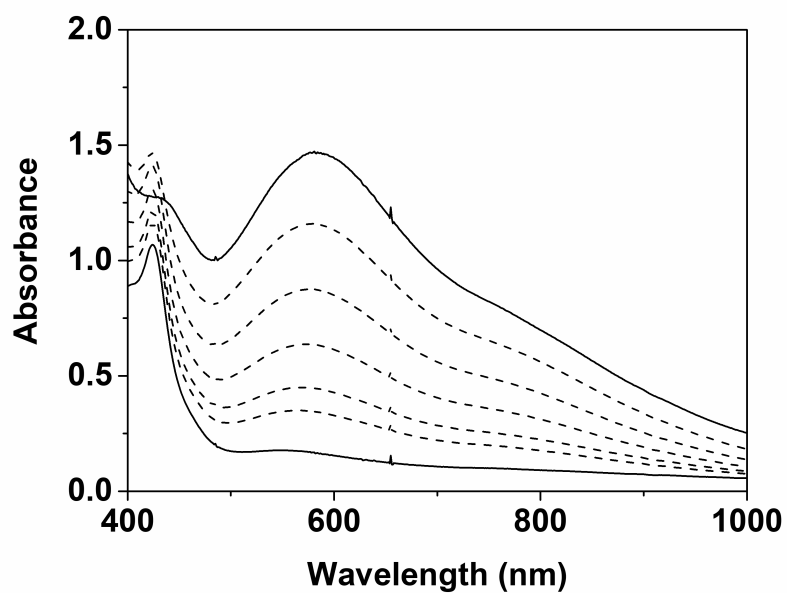


Figure A.92. Changes in the electronic absorption spectrum during the decay of **52b** in the presence of 100 equivalents of 2,6-DTBP.

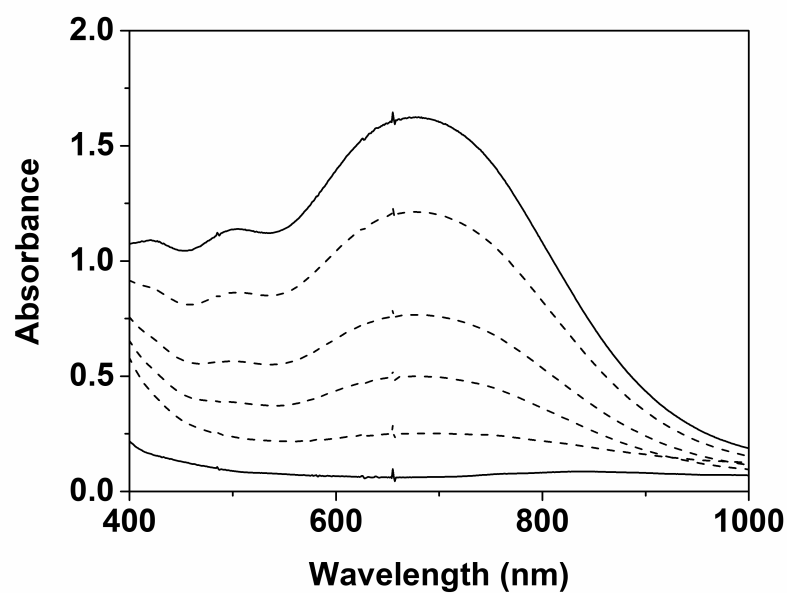


Figure A.93. Changes in the electronic absorption spectrum during the decay of **53b** in the presence of 50 equivalents of 2,6-DTBP.

A.4 Chapter 5

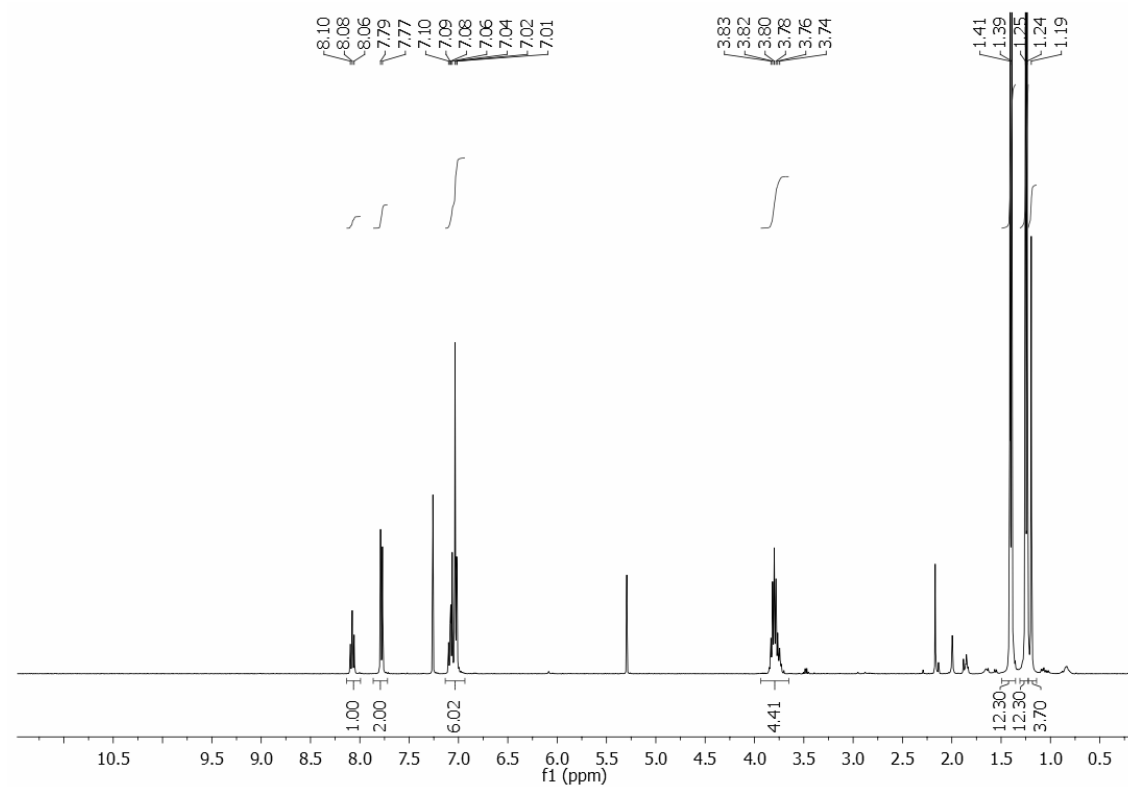


Figure A.94. ¹H NMR spectrum of **56** (400 MHz, CDCl₃).

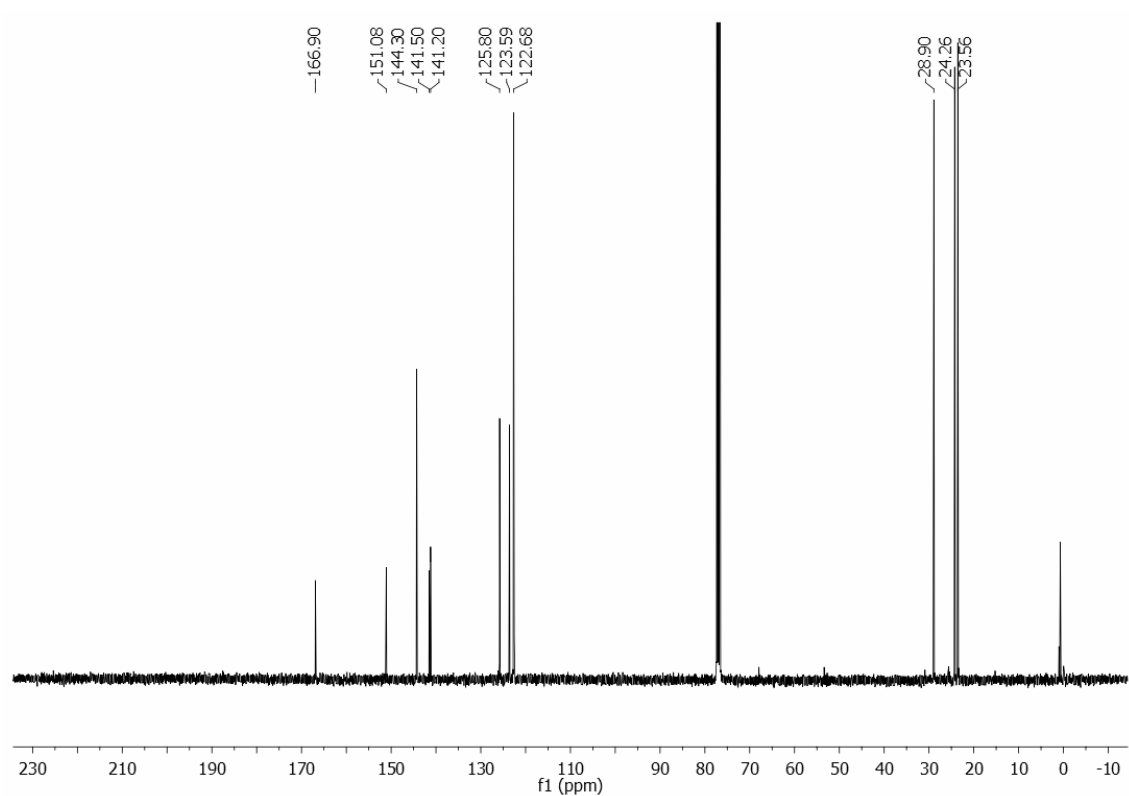


Figure A.95. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **56** (101 MHz, CDCl_3).

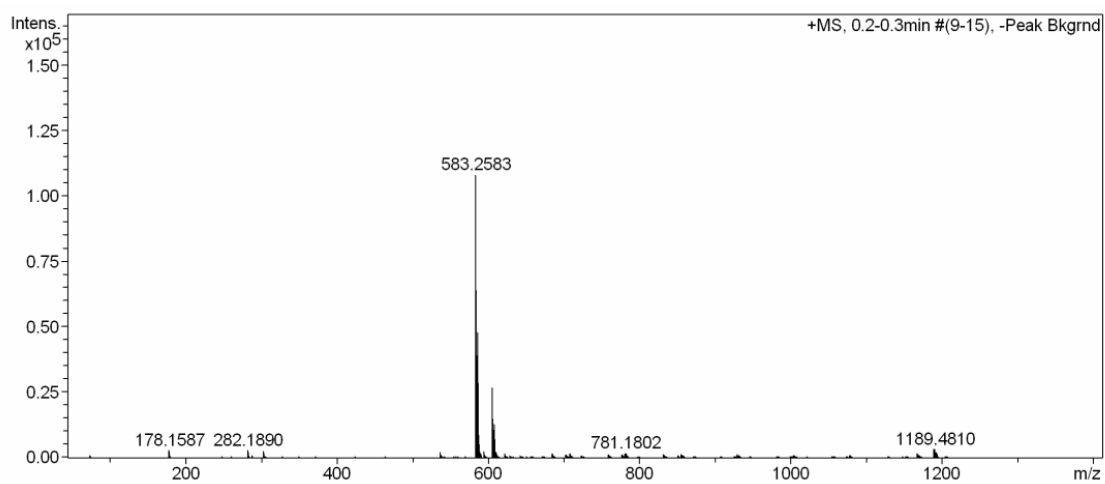


Figure A.96. Positive mode ESI MS spectrum of **56**.

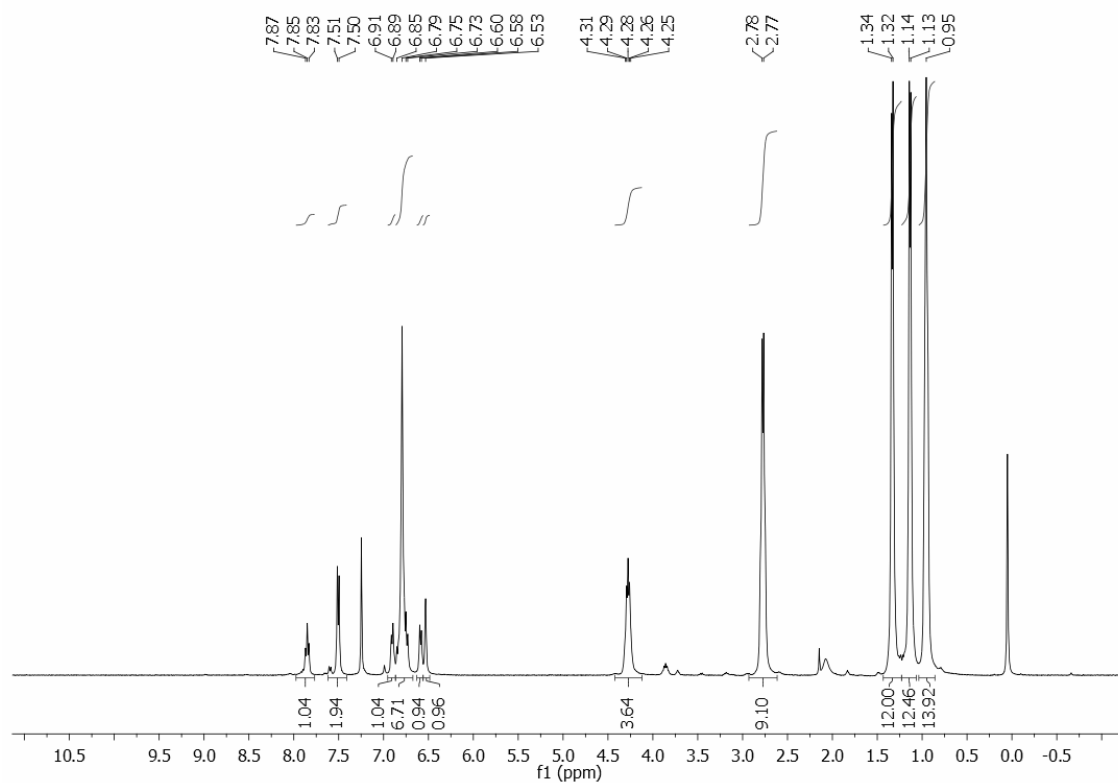


Figure A.97. ^1H NMR spectrum of **57a** (400 MHz, CDCl_3).

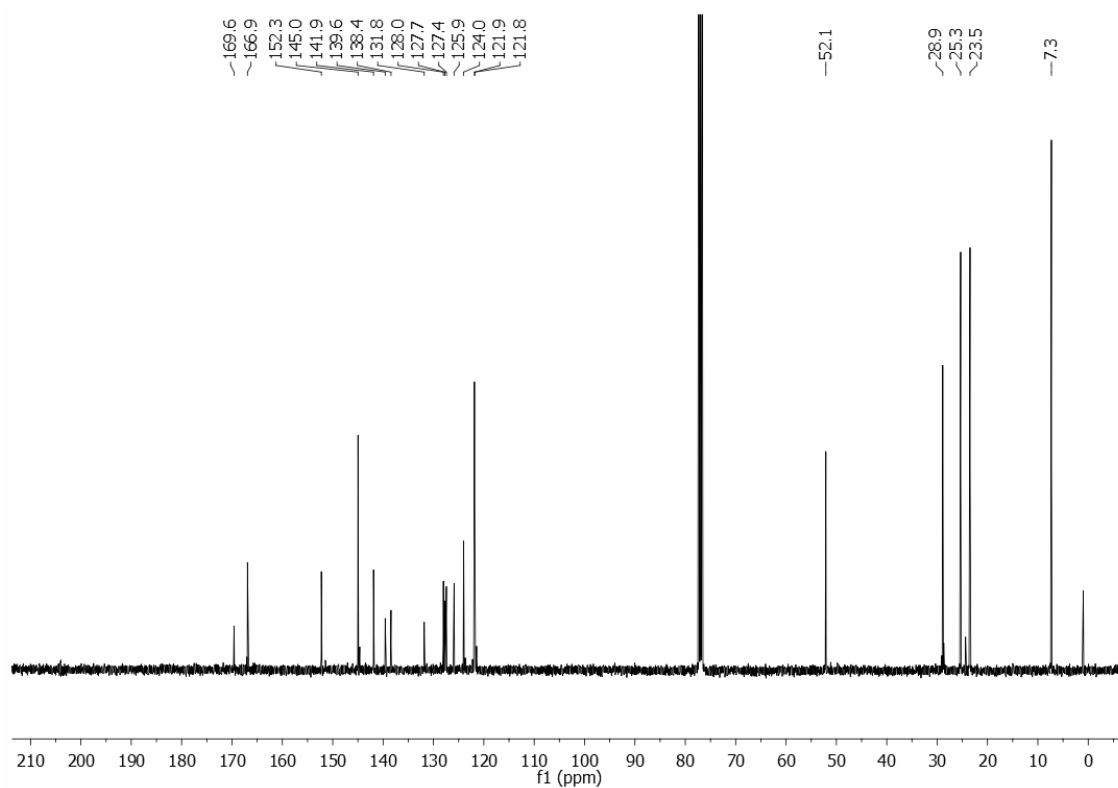


Figure A.98. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **57a** (101 MHz, CDCl_3).

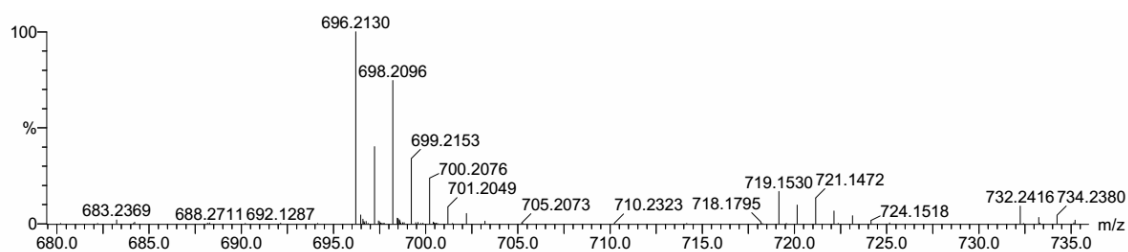


Figure A.99. Negative mode ESI MS spectrum of **57a**.

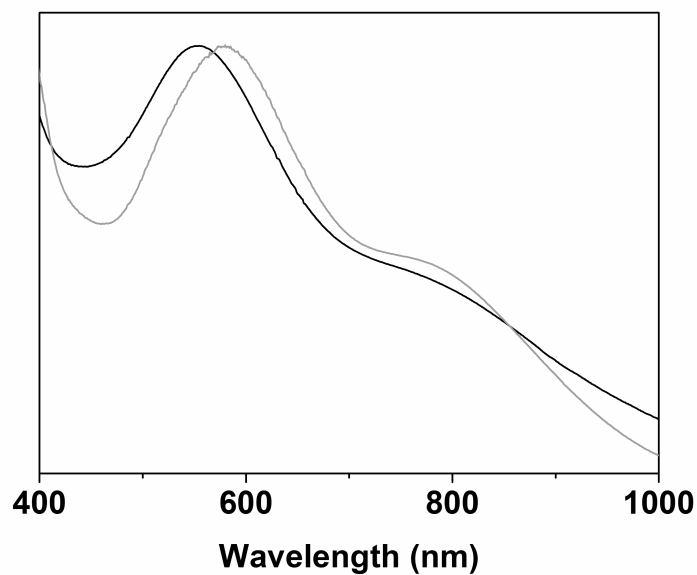


Figure A.100. Normalised UV-Vis spectra of the products obtained from the reaction of **56** and *m*-CPBA (black trace) and of **57a** and magic blue (grey trace).

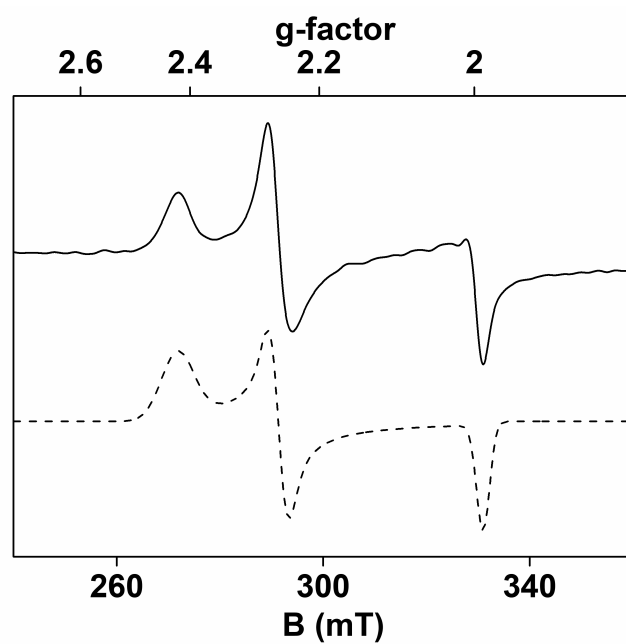


Figure A.101. X-Band EPR spectrum of **57b**, formed by the reaction of **57a** with 1 equiv. magic blue (top) and simulated spectrum (bottom). Measured at 77 K in frozen acetone solution, 2 mW microwave power.

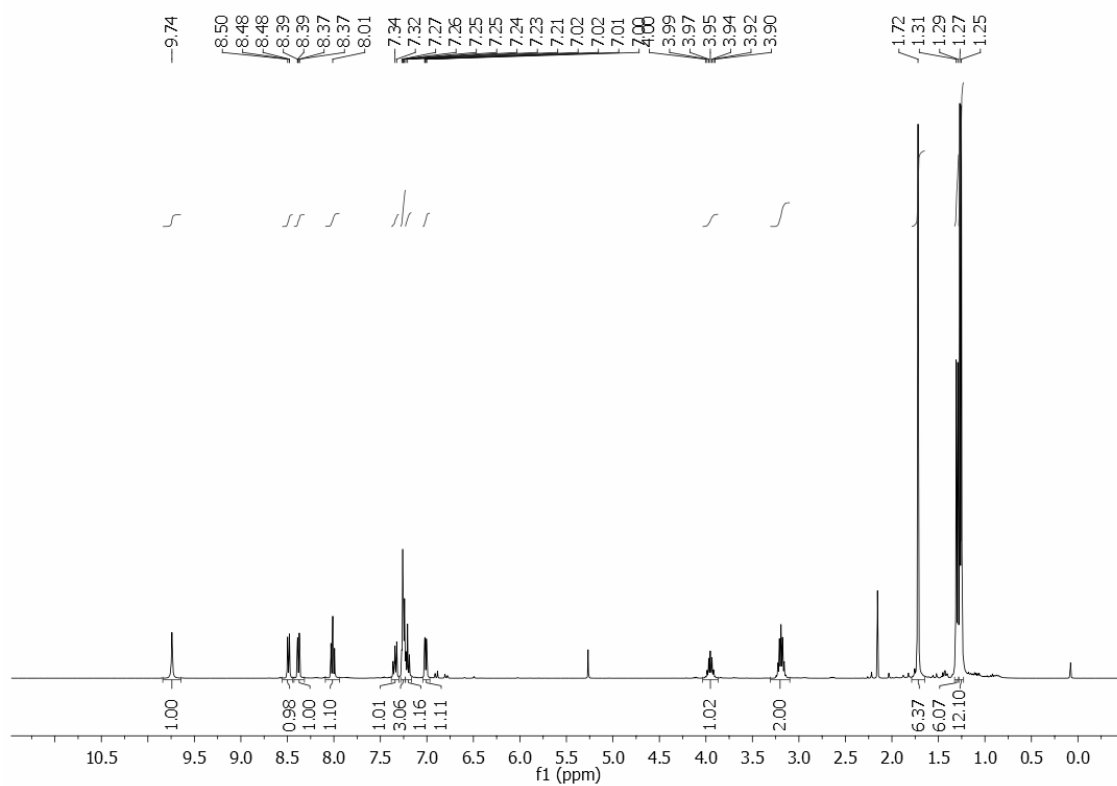


Figure A.102. ¹H NMR spectrum of **58** (400 MHz, CDCl₃).

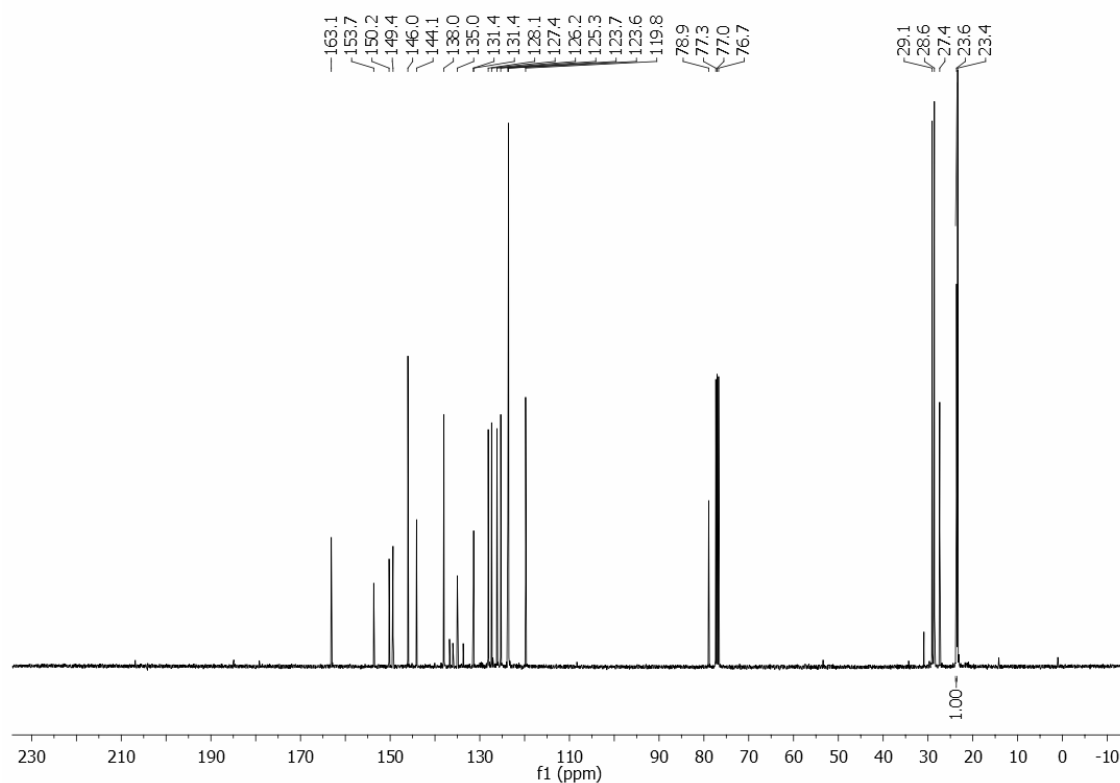


Figure A.103. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **58** (101 MHz, CDCl_3).

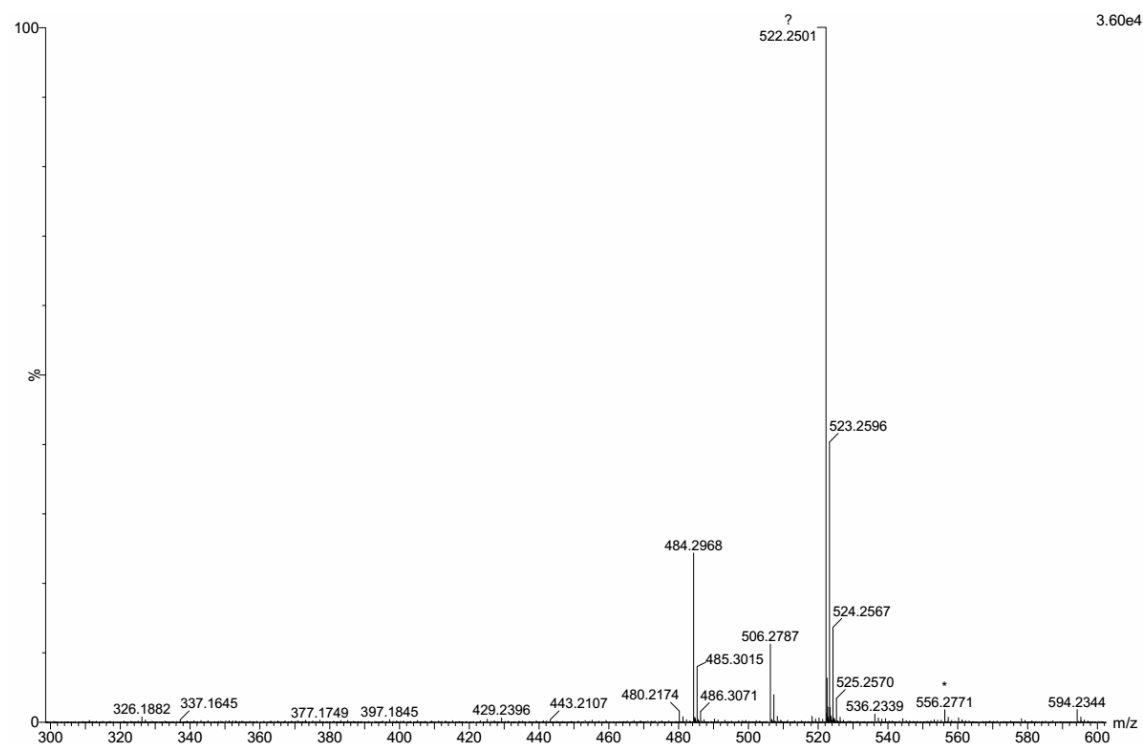


Figure A.104. Positive mode ESI MS spectrum of **58**.

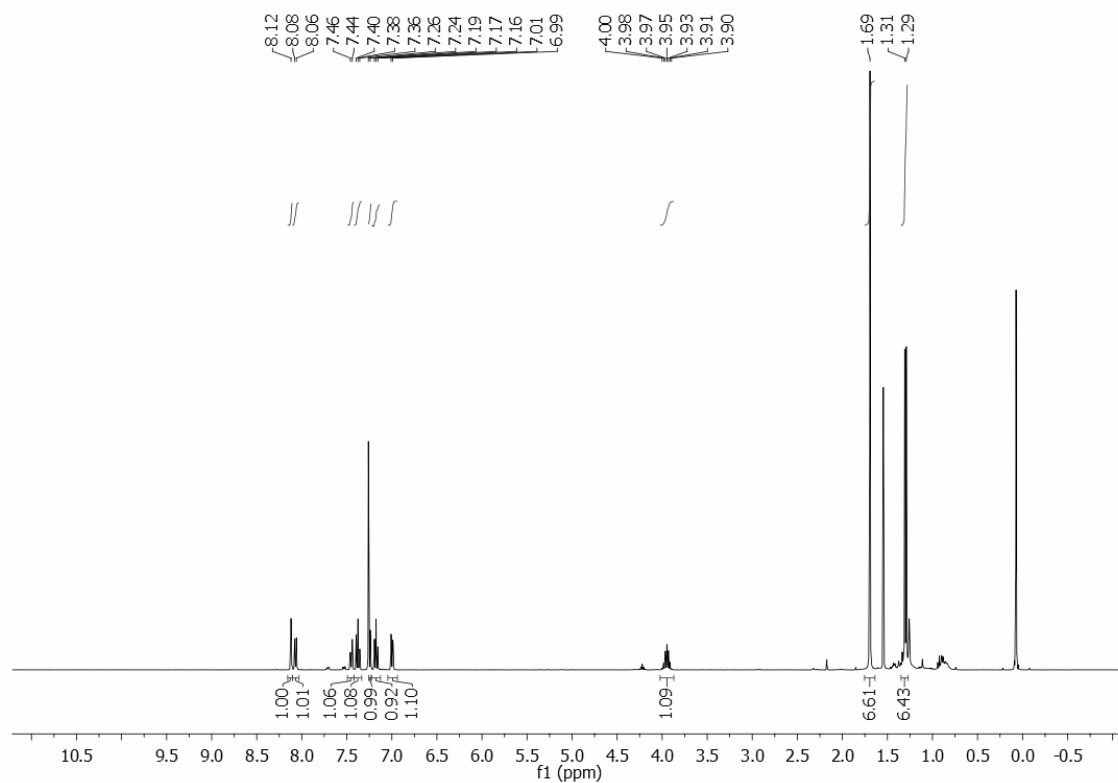


Figure A.105. ^1H NMR spectrum of **59** (400 MHz, CDCl_3).

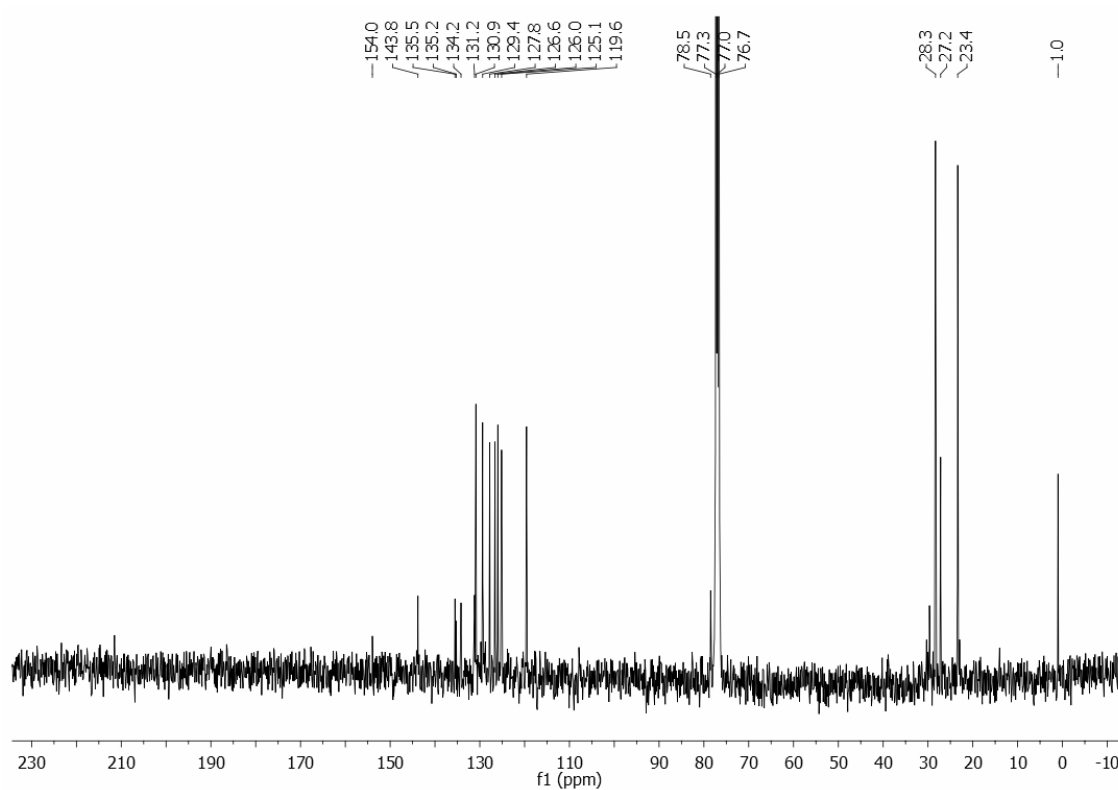


Figure A.106. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **59** (101 MHz, CDCl_3).

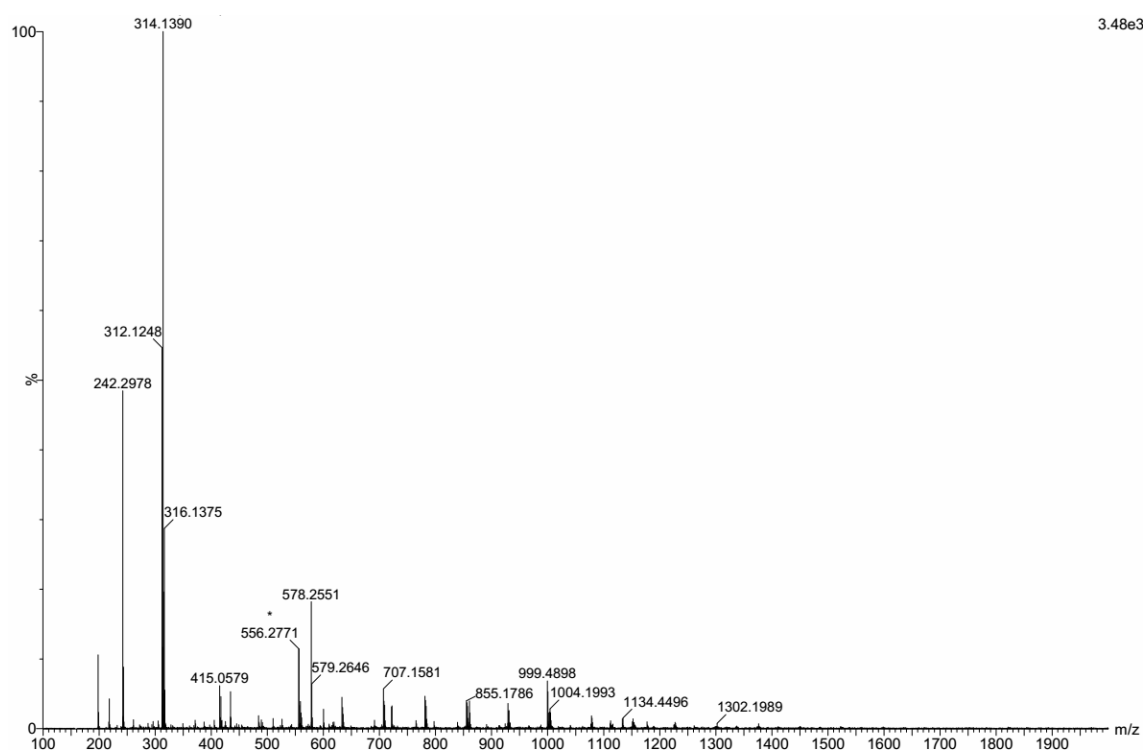


Figure A.107. Positive mode ESI MS spectrum of **59**.

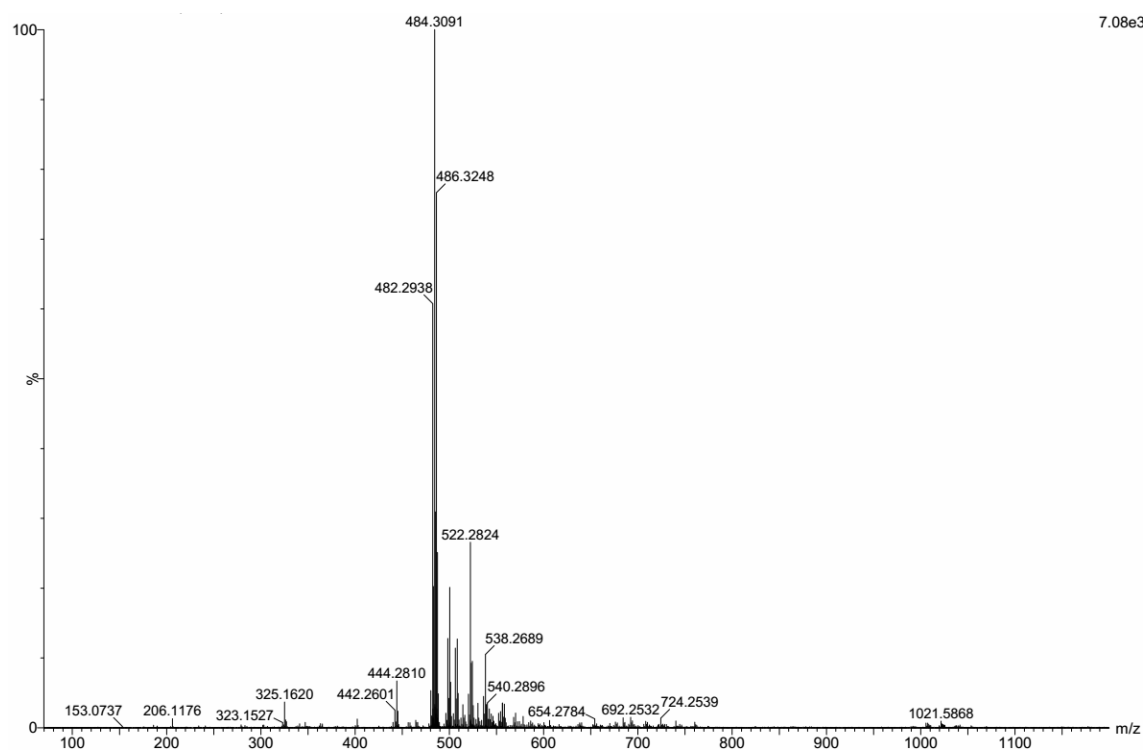


Figure A.108. Positive mode ESI-MS spectrum of the post-decay (**56** + *m*-CPBA) mixture.

A.5 Chapter 6

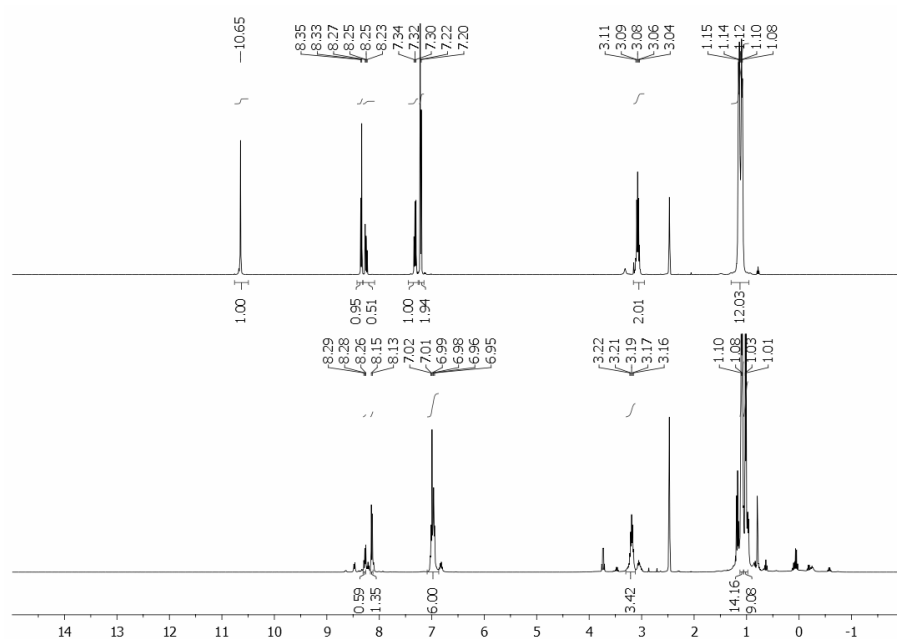


Figure A.109. ^1H NMR spectra of (top) $\text{H}_2\text{pyN}_2^{\text{iPr}_2}$ and (bottom) **65** (400 MHz, $[\text{D}_6]\text{DMSO}$).

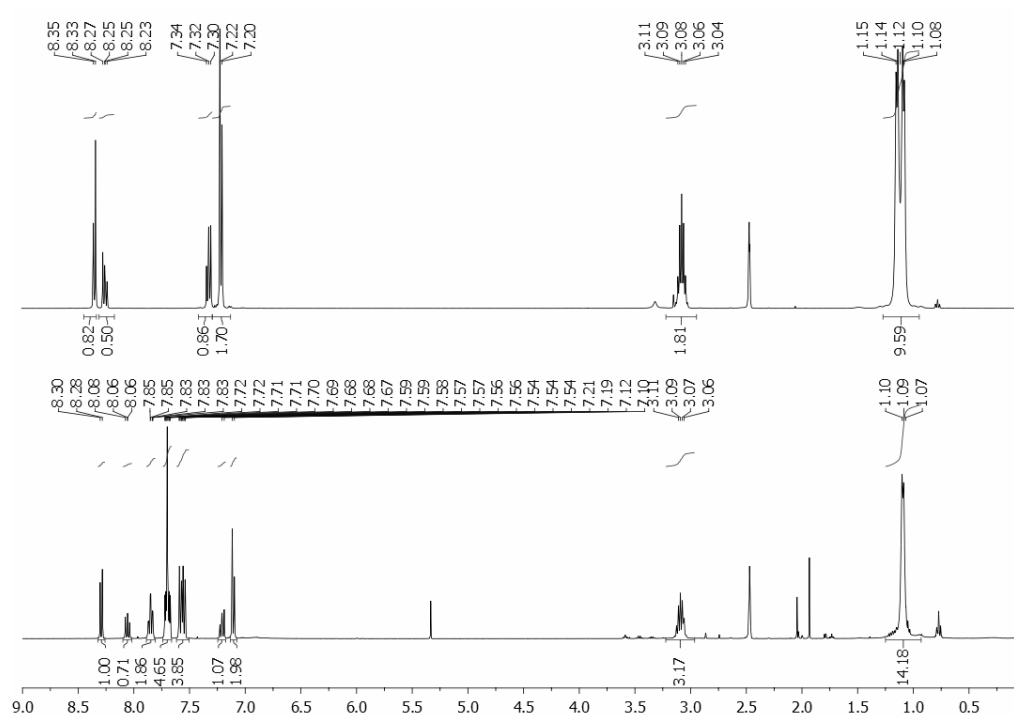


Figure A.110. ^1H NMR spectra of (top) $\text{H}_2\text{pyN}_2^{\text{iPr}_2}$ and (bottom) **64** (400 MHz, $[\text{D}_6]\text{DMSO}$).

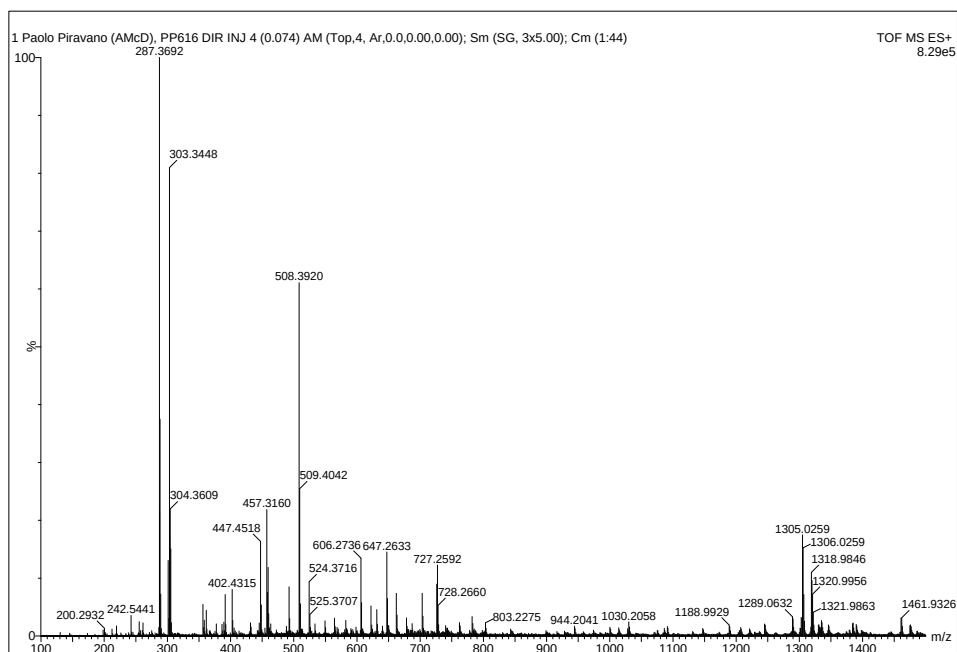


Figure A.111. Positive mode ESI MS spectrum of **62**.

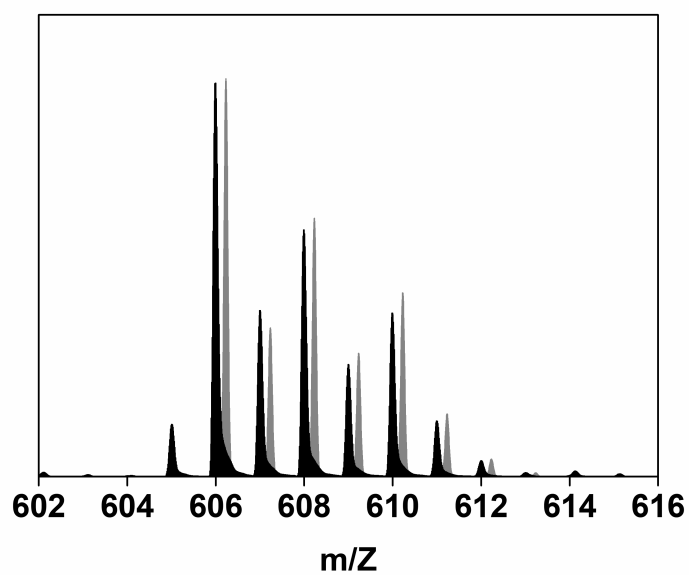


Figure A.112. Experimental (black) and simulated (grey) negative mode ESI MS spectra of **63**.

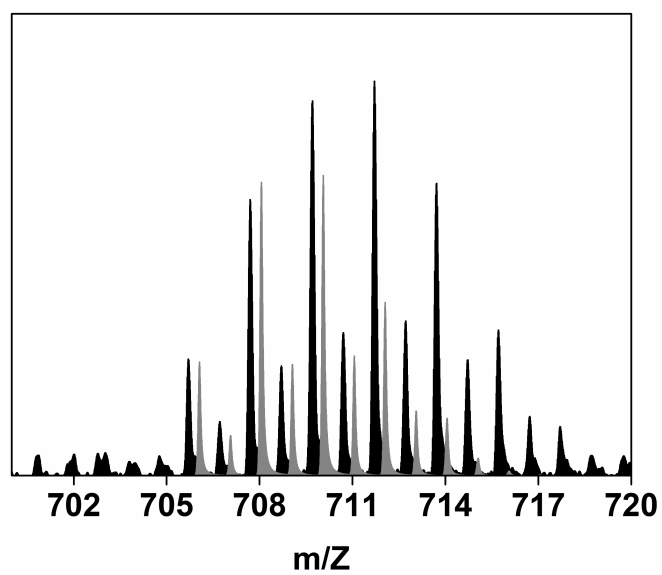


Figure A.113. Experimental (black) and simulated (grey) negative mode ESI MS spectra of **64**.

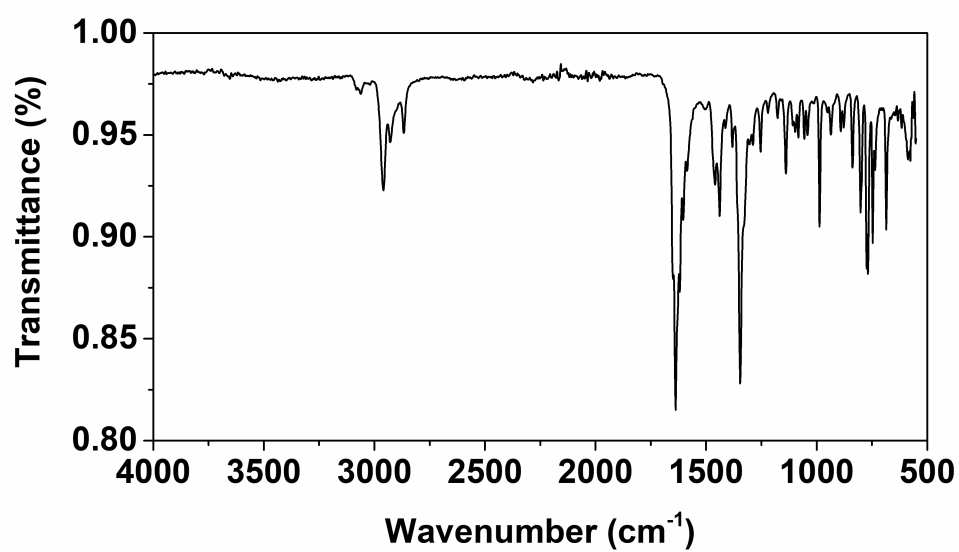


Figure A.114. ATR-FTIR spectrum of **62**.

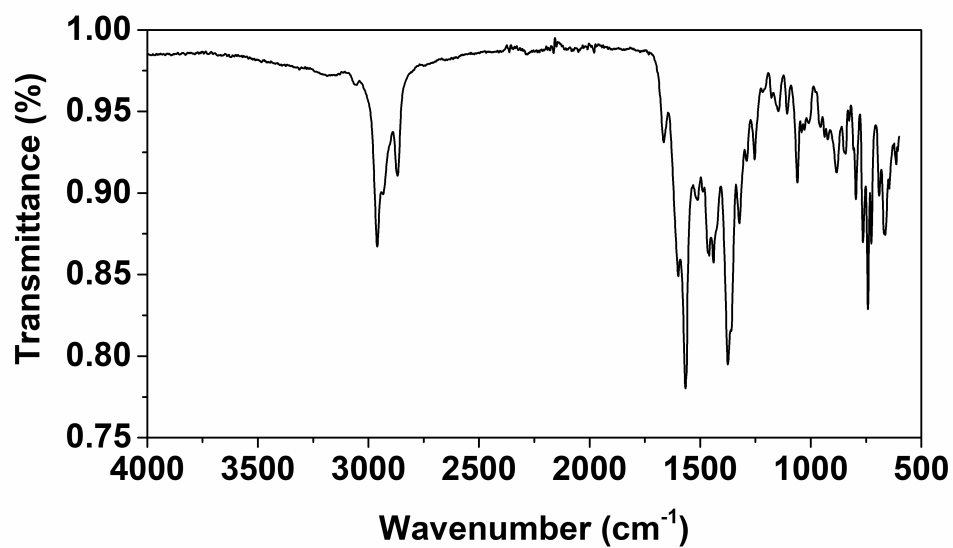


Figure A.115. ATR-FTIR spectrum of **63**.