Elucidating the Electronic Structure of Transition Metal Complexes Featuring Redox Active Ligands

by
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Abstract

In this thesis a number of projects involving the design and characterization of complexes bearing redox active ligands are described. Focusing on the phenolate containing ligands, the properties and electronic structure of their corresponding metal complexes were studied by a series of experimental (i.e. electrochemistry, UV-Vis-NIR, EPR, rR etc.) and theoretical (DFT) methods. Specifically, the redox processes of these metal complexes were tuned by varying the para-ring substituents. In one study, nickel-salen (salen is a common abbreviation for N₂O₂ bis-Schiff-base bis-phenolate ligands) complexes were investigated, where the oxidation potentials of the ligand were predictably decreased as the electron donating ability of the para-ring substituents was increased (NMe₂ > OMe > tBu > CF₃). Interestingly, the oxidation of these geometrically-symmetric complexes afforded an asymmetric electronic structure in a number of cases, in which the ligand radical was localized on one phenolate rather than delocalized across the ligand framework. This difference in electronic structure was found to be dependent on the electron donating ability of the substituents; a delocalized ligand radical was observed for electron-withdrawing substituents and a localized ligand radical for strongly donating substituents. These studies highlight that para-ring substituents can be used to tune the electronic structure (metal vs. ligand based, localized vs. delocalized radical character) of metallosalen complexes. To evaluate if this electronic tuning can be applied to the metal center, a series of cobalt complexes of these salen ligands were prepared. Indeed, the electronic properties of the metal center were also significantly affected by para-ring substitution. These cobalt-salen complexes were tested as catalysts in organometallic radical-mediated polymerizations, where the most electron rich complexes displayed the best conversion rates. With a firm understanding of the role that the para-ring substituent can play in influencing the electronic structure and reactivity of metallosalen complexes in catalysis, two novel iron complexes, which contain a number of redox active phenolate fragments, were prepared. In addition, these iron-complexes feature a chiral bipyrrrolidine backbone. Ligands with this chiral diamine backbone bind metals ions diastereoselectively owing to its increased rigidity, which is critical to stereoselectivity in catalysis. A symmetric (with two phenolates) ligand was prepared by reported methods, and a novel route to synthesize an asymmetric ligand (one phenolate and one pyridine) from symmetric starting materials was established. The neutral iron-complexes were found to be high spin (S = 5/2), and can undergo ligand based oxidation to form an antiferromagnetically-coupled (S_total = 2) species. The results presented will serve as the basis for catalyst development using complexes of similar ligands.
Keywords: Redox Active Ligands; Ligand Design; Transition Metal Complexes; Oxidation; Electronic Structure; Catalysis.
Dedication

To my family, friends and colleagues. None of this would have been possible without any of you. And for that I can't thank you enough.
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A thesis (especially this one) is not representative of the work done by just one person. There have been so many people that have helped me along the way in the past five years; I’ll try to do them justice in the space below.

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# Table of Contents

Approval.............................................................................................................................ii
Partial Copyright Licence .................................................................................................. iii
Abstract.............................................................................................................................iv
Dedication.........................................................................................................................vi
Acknowledgements.......................................................................................................... vii
Table of Contents..............................................................................................................ix
List of Tables .................................................................................................................... xii
List of Figures.................................................................................................................. xiv
List of Schemes............................................................................................................... xix
List of Acronyms...............................................................................................................xx

## Chapter 1. Introduction

1.1 Coordination Chemistry ...............................................................................................1
1.2 Redox Active Ligands .................................................................................................3
1.3 Redox Active Ligands in Nature ..................................................................................5
1.4 Synthetic Models Containing Redox Active Ligands .................................................12
  1.4.1 Dithiolenes .................................................................................................... 12
  1.4.2 Dioxolenes (Quinones) .................................................................................. 14
  1.4.3 Bipyridines and other α-Diimines .................................................................. 17
  1.4.4 Salens and other Phenol Containing Ligands ...............................................19
1.5 Redox Active Ligands in Catalysis ............................................................................ 22
1.6 Thesis Synopsis ........................................................................................................ 23
1.7 References................................................................................................................ 24

## Chapter 2. Ligand Radical Localization of Symmetric One-Electron Oxidized Nickel Salen Complexes

2.1 Introduction ............................................................................................................... 40
2.2 Experimental ............................................................................................................. 44
  2.2.1 Materials ........................................................................................................ 44
  2.2.2 Instrumentation .............................................................................................. 44
    2.2.2.1 General .................................................................................................. 44
    2.2.2.2 Continuous Wave EPR ......................................................................... 45
    2.2.2.3 Pulsed EPR ........................................................................................... 45
    2.2.2.4 Resonance Raman ............................................................................... 46
  2.2.3 Oxidation Protocols ....................................................................................... 46
  2.2.4 Calculations ................................................................................................... 46
  2.2.5 Synthesis ....................................................................................................... 47
2.3 Results and Discussion............................................................................................. 48
  2.3.1 Synthesis ....................................................................................................... 48
  2.3.2 Electrochemistry ............................................................................................ 49
  2.3.3 Theoretical Characterization ......................................................................... 52
    2.3.3.1 Theoretical Characterization ................................................................. 52
    2.3.3.2 Electronic Structures ............................................................................. 54
  2.3.4 Continuous Wave Electron Paramagnetic Resonance ........................................ 56
List of Tables

Table 2.1. Redox Potentials for Ni(Sal)$^R$ versus Fc$^*/$Fc$^-$.43 ...................................................... 50
Table 2.2. Experimental and calculated coordination sphere metrical parameters for neutral Ni(Sal)$^R$ in Å. ......................................................................................... 53
Table 2.3. Experimental and calculated coordination sphere metrical parameters for oxidized [Ni(Sal)$^R$]$^{+\cdot}$ in Å. ............................................................. 54
Table 2.4. B3LYP and CAM-B3LYP predicted spin density values for [Ni(Sal)$^R$]$^{+\cdot}$. ........................................................................................................ 55
Table 2.5. Correlation of X-band EPR isotropic g-values with predicted spin density on Ni for [Ni(Sal)$^R$]$^{+\cdot}$. ......................................................................................... 59
Table 2.6. Band Shape Parameters for NIR transitions of [Ni(Sal)$^R$]$^{+\cdot}$. ........................................ 66
Table 2.7. Comparison of the experimental and calculated TD-DFT NIR transitions for [Ni(Sal)$^R$]$^{+\cdot}$ using the B3LYP and CAM-B3LYP functional. ................................................................................................ 68
Table 3.1. Experimental coordination sphere metrical parameters for M(Sal)CF$_3$ in comparison to other known M(Sal)$^R$ complexes in Å. .................. 84
Table 3.2. Redox Potentials for Ni(Sal)$^R$ versus Fc$^*/$Fc.8 .................................................................. 85
Table 3.3. Redox Potentials for Cu(Sal)$^R$ versus Fc$^*/$Fc.8 .......................................................... 87
Table 3.4. Observed NIR transitions, experimental $\Delta\nu_{1/2}$, and calculated $\Delta\nu_{1/2}$ based on the Hush equation for [Ni(Sal)$^{t\cdot}$Bu]$^{+\cdot}$ and [Ni(Sal)CF$_3$]$^{+\cdot}$. .......... 89
Table 3.5. X-band EPR simulation parameters for the Ni complex ..................................................... 93
Table 3.6. X-band EPR simulation parameters for Cu(Sal)CF$_3$. .................................................. 94
Table 3.7. Calculated coordination sphere metrical parameters for Ni(Sal)CF$_3$ and [Ni(Sal)CF$_3$]$^{+\cdot}$ in Å. ............................................................................................ 95
Table 3.8. Experimental and calculated coordination sphere metrical parameters for Cu(Sal)CF$_3$ and [Cu(Sal)CF$_3$]$^{+\cdot}$ in Å. See Figure 4.4 for atom numbering. .................................................. 96
Table 3.9. Observed NIR transitions and their theoretical analysis for [Ni(Sal)$^{t\cdot}$Bu]$^{+\cdot}$ and [Ni(Sal)CF$_3$]$^{+\cdot}$ ................................................................. 99
Table 4.1. Redox Potentials for Co(Sal)$^R$ versus Fc$^*/$Fc.53 ......................................................... 114
Table 4.2. Co 2p$_{3/2}$ and 2p$_{1/2}$ binding energies by X-ray photoelectron spectroscopy (XPS). .............................................................................................. 117
Table 4.3. X-band EPR simulation parameters for Co(Sal)$^R$. ....................................................... 119
Table 4.4. Experimental and theoretical coordination sphere metrical parameters for Co(Sal)$^{NO_2}$-THF in Å. See Figure 4.4 for atom numbering .................................................. 119
Table 4.5. Styrene polymerization data for Co(Sal)$^R$ at 120°C ...................................................... 122
Table 4.6. Styrene polymerization data for Co(Sal)\textsuperscript{Bu} and Co(Sal)\textsuperscript{NO2} at 65°C .................................................................................................................. 123
Table 4.7. Vinyl acetate polymerization data for Co(Sal)\textsuperscript{R} at 120°C. ..................... 127
Table 5.1. Experimental and calculated coordination sphere metrical parameters for FeL\textsuperscript{1}Cl and [FeL\textsuperscript{1}Cl]\textsuperscript{+} in Å. ................................................................. 147
Table 5.2. Experimental and calculated coordination sphere metrical parameters for FeL\textsuperscript{2}Cl\textsubscript{2} and [FeL\textsuperscript{2}Cl\textsubscript{2}]\textsuperscript{+} in Å. .................................................. 148
Table 5.3. Redox Potentials for Fe complexes versus Fc\textsuperscript{+}/Fc. ............................... 153
Table 5.4. Spectroscopic properties of Fe complexes in CH\textsubscript{2}Cl\textsubscript{2} at 195 K. .......... 155
Table 6.1. Preliminary oxidative catalysis of cyclohexane by Fe catalysts. ...................... 177
Table 6.2. C-H Bond Dissociation Energies of potential substrates of interest. \textsuperscript{19} .................................................................................................................. 178
List of Figures

Figure 1.1. Original and revised structures of cobalt complexes studied by Werner................................................................. 2
Figure 1.2. Structures of cis-platin, Wilkinson’s catalyst, and Grubbs catalyst. .......... 3
Figure 1.3. Possible oxidation processes for metal complexes with redox active ligands. Red dotted electron symbolizes electron lost in the oxidation. ...................................................................................................... 4
Figure 1.4. Possible reduction processes for metal complexes with redox active ligands. Red electron symbolizes electron gained in the reduction........................................................................................................ 5
Figure 1.5. O₂ as a redox active ligand, and examples of O₂ ambi-valence in bioinorganic chemistry, specifically in heme-based⁷²-⁷³ and Cu-based oxygen transport proteins.⁸³ ............................................................... 7
Figure 1.6. NO as a redox active ligand, and its different bonding modes to metal ions. ................................................................................................................................................................................. 8
Figure 1.7. Mechanism of action for Galactose Oxidase. ............................................................. 9
Figure 1.8. Active site of Galactose Oxidase.¹⁰⁹ ............................................................................. 10
Figure 1.9. Active site of cytochrome P450.¹¹² .............................................................................. 11
Figure 1.10. Mechanism of action of cytochrome P450.......................................................... 12
Figure 1.11. Early examples of bis(dithiolene) complexes by Schrauzer and Mayweg¹¹³, Gray and co-workers¹¹⁴-¹¹⁵, and Davison and co-workers.¹¹⁶ .............................................................. 13
Figure 1.12. General structure of tris(dithiolene) complexes. ................................................. 14
Figure 1.13. Examples of quinones in Nature........................................................................ 14
Figure 1.14. Different oxidation states of ortho-benzoquinones........................................... 15
Figure 1.15. Iron containing catechol dioxygenase and copper containing amine oxidase. ............................................................................................................................. 15
Figure 1.16. Valence tautomerism of a Co complex.¹⁵⁵ ............................................................. 16
Figure 1.17. Dioxolene and its N,O (iminoquinone) and N,N (diimine) derivatives. .............................................................. 17
Figure 1.18. Bipyridine ligand, and various oxidation states of 2,2’-bipyridine and 1,4-diazabutadiene................................................................. 18
Figure 1.19. Different oxidation states and corresponding bonding distances (in Å) of α-iminopyridines.¹⁸⁸,¹⁹⁰ ..................................................................................... 18
Figure 1.20. Other nitrogen containing redox active ligands. ............................................. 19
Figure 1.21. Phenol containing redox active ligands. ............................................................ 20
Figure 1.22. Synthesis of Salen ligands and analogues......................................................... 21
Figure 1.23. Phenolate vs. phenoxy ligand bond distances (in Å). ........................................... 22
Figure 2.1. Structures of NiII-salen complexes (Ni(Sal)R). .................................................. 41
Figure 2.2. Hush model of an IVCT, where the two harmonic ground states (dotted lines) are coupled to form low and high energy surfaces (solid lines). ........................................................................................................ 42
Figure 2.3. Structure of the Creutz-Taube ion. ....................................................................... 43
Figure 2.4. Cyclic Voltammograms of: (a) Ni(Sal)Bu, (b) Ni(Sal)OMe and (c) Ni(Sal)NMe2 in CH2Cl2 at 233 K. ........................................................................................................ 50
Figure 2.5. Calculated spin density using the B3LYP functional for: (a) [Ni(Sal)Bu]+, (b) [Ni(Sal)OMe]+ and (c) [Ni(Sal)NMe2]+. Calculated spin density using the CAM-B3LYP functional for: (d) [Ni(Sal)Bu]+, (e) [Ni(Sal)OMe]+ and (f) [Ni(Sal)NMe2]+. .................................................. 55
Figure 2.6. DFT-optimized structure of [Ni(Sal)NMe2]+ ......................................................... 56
Figure 2.7. X-band EPR spectra for: [Ni(Sal)Bu]+ (black), [Ni(Sal)OMe]+ (red) and [Ni(Sal)NMe2]+ (blue) in CH2Cl2 at 20 K. .............................................................................. 57
Figure 2.8. X-band EPR spectra for: (a) [Ni(Sal)Bu]+, (b) [Ni(Sal)OMe]+ and (c) [Ni(Sal)NMe2]+ in CH2Cl2 at 298 K. .................................................................................. 58
Figure 2.9. 2D-HYSCORE spectra of [Ni(Sal)Bu]+ at the g = 2.045 value of the continuous-wave spectrum in CH2Cl2 at 4 K. Insert: Magnification of the (+,+ ) quadrant.............................................. 60
Figure 2.10. 2D-HYSCORE spectra of [Ni(Sal)OMe]+ at the g = 2.023 value of the continuous-wave spectrum in CH2Cl2 at 4 K. Insert: Magnification of the (+,+ ) quadrant.............................................. 61
Figure 2.11. 2D-HYSCORE spectra of [Ni(Sal)NMe2]+ at the g = 2.005 value of the continuous-wave spectrum in CH2Cl2 at 4 K........................................................................... 62
Figure 2.12. Resonance Raman spectra for: (a) Ni(Sal)OMe (black) and [Ni(Sal)OMe]+ (red) and (b) Ni(Sal)NMe2 (black) and [Ni(Sal)NMe2]+ (red). .................................................................................. 63
Figure 2.13. UV-Vis-NIR spectrum of Ni(Sal)Bu (black) and [Ni(Sal)Bu]+ (red) in CH2Cl2 at 298 K. ............................................................................................................................... 64
Figure 2.14. UV-Vis-NIR spectrum of Ni(Sal)OMe (black) and [Ni(Sal)OMe]+ (red) in CH2Cl2 at 298 K ....................................................................................................................................... 65
Figure 2.15. UV-Vis-NIR spectrum of Ni(Sal)NMe2 (black) and [Ni(Sal)NMe2]+ (red) in CH2Cl2 at 298 K .................................................................................................................. 65
Figure 2.16. Variable Temperature UV-Vis-NIR spectrum of [Ni(Sal)NMe2]+ in CH2Cl2. ................................................................................................................................. 67
Figure 2.17. Kohn Sham Molecular Orbitals associated with the predicted NIR transitions by TD-DFT calculations using the CAM-B3LYP functional for: (a) [Ni(Sal)]^**; (b) [Ni(Sal)]^** and (c) [Ni(Sal)]^**. ..............................

Figure 3.1. POV-Ray representation of Ni(Sal)^CF3 ..............................................................

Figure 3.2. POV-Ray representation of Cu(Sal)^CF3 ..............................................................

Figure 3.3. Cyclic voltammogram (solid line) and differential pulse voltammogram (dotted line) of Ni(Sal)^CF3 in CH2Cl2 at 298 K ..........

Figure 3.4. Hamnett plot of the first oxidation potential (V) of Ni(Sal)^R. σpara values from 32. ..............................................................

Figure 3.5. Cyclic Voltammogram of Cu(Sal)^CF3 in CH2Cl2 at 298 K ..........

Figure 3.6. UV-Vis-NIR spectrum of Ni(Sal)^CF3 (black), [Ni(Sal)^CF3]^** (red) and [Ni^III(Sal)^CF3(py)2]^** (blue) at 0.4 mM in CH2Cl2 at 198 K ..........

Figure 3.7. UV-Vis-NIR spectrum of Cu(Sal)^CF3 (black) and [Cu(Sal)^CF3]^* (red) at 0.4 mM in CH2Cl2 at 198 K. ..............................................................

Figure 3.8. VT UV-Vis-NIR spectrum of [Cu(Sal)^CF3]^* at 0.4 mM in CH2Cl2. ..........

Figure 3.9. X-band EPR spectra for: (a) [Ni(Sal)]^** at 195 K; (b) [Ni(Sal)]^** at 20 K and (c) [Ni^III(Sal)]^** at 20 K in CH2Cl2. ....

Figure 3.10. X-band EPR spectra for concentration matched samples of: (a) Cu(Sal)^CF3 and (b) [Cu(Sal)]^** in CH2Cl2 at 20 K. ..............................................................

Figure 3.11. Calculated spin density of Ni(Sal)^CF3 using the B3LYP functional and a polarized continuum model for CH2Cl2 ..........

Figure 3.12. Calculated spin density of Cu(Sal)^CF3 using the B3LYP functional and a polarized continuum model for CH2Cl2. ..............................................................

Figure 3.13. Kohn Sham Molecular Orbitals associated with the predicted NIR transitions by TD-DFT calculations using the B3LYP functional with a polarized continuum model (PCM) for CH2Cl2 for (a) Ni(Sal)^** and (b) Ni(Sal)^**. ..............................................................

Figure 4.1. Structures of Co^II-salen complexes (Co(Sal)^R). ..............................................................

Figure 4.2. Co complexes of different ligands studied for OMRP. ..............................................................

Figure 4.3. Monomers and initiators used in the studies in this Chapter. ..............................................................

Figure 4.4. POV-ray representation of Co(Sal)^NO2*THF. ..............................................................

Figure 4.5. Cyclic voltammograms of Co(Sal)^R: (a) R = NO2; (b) R = tBu; (c): R = OMe; (d): R = NMe2 in CH2Cl2 at 298 K. ..............................................................

Figure 4.6. X-ray photoelectron spectroscopy (XPS) spectra of Co(Sal)^R, specifically showing the Co 2p3/2 and 2p1/2 binding energies (Red: R = NO2; Black: R = tBu; Blue: R = OMe; Green: R = NMe2). ..............................................................

Figure 4.7. X-band EPR spectra of 1 mM frozen solutions of Co(Sal)^R at 20 K. ....
Figure 4.8. Predicted singularly occupied molecular orbital for: a) Co(Sal)NMe2; b) Co(Sal)OMe; c) Co(Sal)Bu and d) Co(Sal)NO2-THF............................... 120

Figure 4.9. Plots of a) ln([M]0/[M]t) vs. time and b) molecular weight vs. conversion for bulk styrene polymerization at 120°C using Co(Sal)Bu and AIBN............................................................................. 124

Figure 4.10. 1H NMR spectrum of polystyrene, showing olefin end-groups at δ = 6.1-6.2 ppm and adjacent methane groups at δ = 3.1 ppm............. 125

Figure 4.11. Plots of a) ln([M]0/[M]t) vs. time and b) molecular weight vs. conversion for bulk styrene polymerization at 120°C using Co(Sal)Bu and AIBN............................................................................. 126

Figure 4.12. GPC traces of crude (red) and worked-up (blue) PMMA samples. ........ 126

Figure 5.1. Phenolate containing ligands employing macrocyclic, linear, and chiral amine backbones............................. 137

Figure 5.2. Symmetric bis-phenol ligand H2L1 and dissymmetric mono-phenol ligand HL2...................................................... 138

Figure 5.3. POV-Ray representation of (S,S)-FeL1Cl.................................................. 147

Figure 5.4. POV-Ray representation of (S,S)-FeL2Cl2........................................ 148

Figure 5.5. Possible binding modes of tetradentate ligands in an octahedral geometry............................................................... 148

Figure 5.6. POV-Ray representations of (a) (S,S)-FeL2Cl2, (Λ helical geometry) and (b) (R,R)-FeL2Cl2 (Δ helical geometry), hydrogen atoms and solvent excluded.......................................................... 149

Figure 5.7. Cyclic voltammograms of (a) H2L1 (black) and FeL1Cl (blue); and (b) HL2 (black) and FeL2Cl2 (blue) in CH2Cl2 at 233 K. ...................... 151

Figure 5.8. Extended cyclic voltammograms of (a) FeL1Cl, and (b) FeL2Cl2 in CH2Cl2 at 233 K................................................................. 152

Figure 5.9. UV-Vis-NIR spectra of (a) FeL1Cl (black), [FeL1Cl]^+ (red), and (b) FeL2Cl2 (black) and [FeL2Cl2]^+ (red) in CH2Cl2 at 195 K.. 154

Figure 5.10. Resonance Raman (rR) spectra of (a) FeL1Cl (black), [FeL1Cl]^+ (red); b) FeL2Cl2 (black), [FeL2Cl2]^+ (red). ............................... 156

Figure 5.11. Perpendicular mode X-band EPR spectra of 0.5 mM solutions of: FeL1Cl (left, (a)), electrochemically generated [FeL1Cl]^+ (left, (b)), FeL2Cl2 (right, (a)), and electrochemically generated [FeL2Cl2]^+ (right, (b)) in frozen CH2Cl2 with 0.1 M nBu4NCIO4 at 10 K. .......................... 157

Figure 5.12. Parallel mode X-band EPR spectrum of a 0.5 mM solution of: (a) electrochemically generated [FeL1Cl]^+ and (b) electrochemically generated [FeL2Cl2]^+ in frozen CH2Cl2 with 0.1 M nBu4NCIO4 at 10 K. ............................................ 158

Figure 5.13. Kohn-Sham molecular orbitals for the broken symmetry (S_total = 2) solution of [FeL2Cl2]^+. ................................................................. 160
Figure 5.14. Kohn-Sham molecular orbitals for the broken symmetry ($S_{\text{total}} = 2$) solution of $[\text{FeL}^1\text{Cl}]^{\text{II}}$. ................................................................. 161

Figure 6.1. Cyclic voltammograms of $\text{Co(Sal)}^R$: (a) $R = \text{tBu}$; (b) $R = \text{OMe}$; (c) $R = \text{NMe}_2$; (d) $R = \text{NO}_2$ versus $\text{Fc}^{+/\text{Fc}}$ (black spectra) with increasing amounts of benzoic acid added (10 mM increments, grey and red spectra) in THF at 298 K. ....................................................... 173

Figure 6.2. POV-Ray representation of $\text{Co(Sal)}^\text{CF}_3$ ...................................................... 175

Figure 6.3. Proposed structure of catalysts with secondary coordination sphere functional groups as either hydrogen bond donors or acceptors. D signifies donors that can guide protons to the catalytic metal site. ........................................................................ 176

Figure 6.4. Structure of $(S,S)$-$\text{Fe(PDP)}$. 17-18 ........................................................................ 177

Figure 6.5. POV-Ray representation of $(R,R)$-$\text{FeL}^2\text{Cl}$. ...................................................... 180

Figure 6.6. POV-Ray representation of $(R,R)$-$\text{FeL}^1\text{N}_3$. ...................................................... 181
### List of Schemes

<table>
<thead>
<tr>
<th>Scheme</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scheme 2.1.</td>
<td>Synthesis of $\text{H}_2(\text{Sal})^{\text{NMe}_2}$ and $\text{Ni}(\text{Sal})^{\text{NMe}_2}$</td>
<td>49</td>
</tr>
<tr>
<td>Scheme 3.1.</td>
<td>Synthesis of $\text{H}_2(\text{Sal})^{\text{CF}_3}$ and $\text{M}(\text{Sal})^{\text{CF}_3}$</td>
<td>82</td>
</tr>
<tr>
<td>Scheme 4.1.</td>
<td>Reversible Termination OMRP (RT-OMRP) mechanism</td>
<td>106</td>
</tr>
<tr>
<td>Scheme 4.2.</td>
<td>Degenerative transfer OMRP (DT-OMRP) mechanism</td>
<td>107</td>
</tr>
<tr>
<td>Scheme 4.3.</td>
<td>Synthesis of $\text{Co}(\text{Sal})^R$</td>
<td>113</td>
</tr>
<tr>
<td>Scheme 4.4.</td>
<td>Catalytic chain transfer (CCT) mechanism</td>
<td>125</td>
</tr>
<tr>
<td>Scheme 5.1.</td>
<td>Formation of Compound I</td>
<td>136</td>
</tr>
<tr>
<td>Scheme 5.2.</td>
<td>Synthesis of $\text{FeL}^1\text{Cl}$ and $\text{FeL}^2\text{Cl}_2$</td>
<td>145</td>
</tr>
<tr>
<td>Scheme 6.1.</td>
<td>Proposed synthesis of $[\text{Ni}^{\text{III}}(\text{Sal})^R(\text{PhIO})_2]^{+}$</td>
<td>171</td>
</tr>
<tr>
<td>Scheme 6.2.</td>
<td>Binding of Axial ligands to $[\text{Ni}^{\text{III}}(\text{Sal})^R]^{	ext{**}}$ and subsequent oxidation</td>
<td>171</td>
</tr>
<tr>
<td>Scheme 6.3.</td>
<td>Oxidation of cyclohexane by Fe catalysts</td>
<td>177</td>
</tr>
<tr>
<td>Scheme 6.4.</td>
<td>Proposed synthesis of Ru analogues</td>
<td>182</td>
</tr>
</tbody>
</table>
List of Acronyms

2D- HYSCORE 2 dimensional-Hyperfine-Sublevel CORrelation Experiment
Å Ångstrom, $10^{-10}$ meters
A Hyperfine coupling constant
AcOH Acetic Acid
AIBN Azobisisobutyronitrile
ATRP Atom Transfer Radical Polymerization
BDE Bond Dissociation Energy
BS Broken Symmetry (DFT)
ºC Degree Celcius
ca. Approximately
Calc Calculated
CCT Catalytic Chain Transfer
cm Centimeters
cm$^{-1}$ Wavenumbers
CT Charge Transfer
CV Cyclic Voltammetry
Cys Cysteine
d Doublet (NMR)
Da Daltons
DFT Density Functional Theory
DPV Differential Pulse Voltammetry
dq Double quantum
DT-OMRP Degenerative Transfer Organometallic Mediated Radical Polymerization
$\Delta \nu_{1/2}$ Peak width at half height
ε Dielectric constant
ε Extinction coefficient (UV-Vis)
E Energy of predicted transition (DFT)
$E_{pa}$ Anodic peak potential
$E_{pc}$ Cathodic peak potential
EPR Electron Paramagnetic Resonance
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ESI</td>
<td>Electrospray ionization</td>
</tr>
<tr>
<td>etc</td>
<td>et cetera</td>
</tr>
<tr>
<td>eV</td>
<td>Electron Volts</td>
</tr>
<tr>
<td>Exp</td>
<td>Experimental</td>
</tr>
<tr>
<td>f</td>
<td>Oscillator strength (DFT)</td>
</tr>
<tr>
<td>F</td>
<td>Faraday’s constant</td>
</tr>
<tr>
<td>Fc</td>
<td>Ferrocene</td>
</tr>
<tr>
<td>Fc+</td>
<td>Ferrocenium</td>
</tr>
<tr>
<td>$g_{av}$</td>
<td>Average $g$ value</td>
</tr>
<tr>
<td>$g_e$</td>
<td>Free electron $g$ value (2.0023)</td>
</tr>
<tr>
<td>GHz</td>
<td>Gigahertz</td>
</tr>
<tr>
<td>$g_{iso}$</td>
<td>Isotropic $g$ value</td>
</tr>
<tr>
<td>GPC</td>
<td>Gel Permeation Chromatography</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>HRMS</td>
<td>High Resolution Mass Spectrometry</td>
</tr>
<tr>
<td>I</td>
<td>Nuclear spin</td>
</tr>
<tr>
<td>IVCT</td>
<td>Intervalence Charge Transfer</td>
</tr>
<tr>
<td>K</td>
<td>Kelvin</td>
</tr>
<tr>
<td>$K_c$</td>
<td>Comproportionation Constant</td>
</tr>
<tr>
<td>kcal/mol</td>
<td>Kilocalories per mole</td>
</tr>
<tr>
<td>kHz</td>
<td>Kilohertz</td>
</tr>
<tr>
<td>Kr</td>
<td>Krypton</td>
</tr>
<tr>
<td>$\lambda_{ex}$</td>
<td>Wavelength of excitation (Resonance Raman)</td>
</tr>
<tr>
<td>$\lambda_{max}$</td>
<td>Wavelength of maximum absorption</td>
</tr>
<tr>
<td>LLCT</td>
<td>Ligand-to-Ligand Charge Transfer</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Bridging atom</td>
</tr>
<tr>
<td>m</td>
<td>Multiplet (NMR)</td>
</tr>
<tr>
<td>M</td>
<td>Metal</td>
</tr>
<tr>
<td>M</td>
<td>Molar (Concentration)</td>
</tr>
<tr>
<td>$\mu A$</td>
<td>Microampere</td>
</tr>
<tr>
<td>$\mu_{eff}$</td>
<td>Effective magnetic moment</td>
</tr>
<tr>
<td>mg</td>
<td>Milligrams</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>µL</td>
<td>Microliters</td>
</tr>
<tr>
<td>$M_i$</td>
<td>Nuclear Spin Angular Momentum</td>
</tr>
<tr>
<td>mL</td>
<td>Milliliters</td>
</tr>
<tr>
<td>mm</td>
<td>Millimeters</td>
</tr>
<tr>
<td>mmol</td>
<td>Millimoles</td>
</tr>
<tr>
<td>$M_n$</td>
<td>Molecular weight of polymer</td>
</tr>
<tr>
<td>$M_{n,th}$</td>
<td>Theoretical Molecular weight of polymer</td>
</tr>
<tr>
<td>MO</td>
<td>Molecular Orbital</td>
</tr>
<tr>
<td>$M_S$</td>
<td>Magnetic spin quantum number</td>
</tr>
<tr>
<td>MS</td>
<td>Mass Spectrometry</td>
</tr>
<tr>
<td>mT</td>
<td>Milliteslas</td>
</tr>
<tr>
<td>mV</td>
<td>Millivolts</td>
</tr>
<tr>
<td>mV s$^{-1}$</td>
<td>Millivolts per second</td>
</tr>
<tr>
<td>mW</td>
<td>Milliwatts</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Vibrational mode (Resonance Raman)</td>
</tr>
<tr>
<td>NHE</td>
<td>Normal Hydrogen Electrode</td>
</tr>
<tr>
<td>$\nu_l$</td>
<td>Larmor Nuclear Frequency</td>
</tr>
<tr>
<td>NIR</td>
<td>Near-Infrared</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometers</td>
</tr>
<tr>
<td>$\nu_{max}$</td>
<td>Energy of maximum absorption</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>OAc</td>
<td>Acetate</td>
</tr>
<tr>
<td>OMRP</td>
<td>Organometallic Mediated Radical Polymerization</td>
</tr>
<tr>
<td>PCM</td>
<td>Polarized Continuum Model</td>
</tr>
<tr>
<td>PDI</td>
<td>Polydispersity Index</td>
</tr>
<tr>
<td>pKa</td>
<td>Acid Dissociation Constant on a logarithmic scale</td>
</tr>
<tr>
<td>PMMA</td>
<td>Poly(methylmethacrylate)</td>
</tr>
<tr>
<td>ppm</td>
<td>Chemical shift</td>
</tr>
<tr>
<td>py</td>
<td>Pyridine</td>
</tr>
<tr>
<td>pyz</td>
<td>Pyrazine</td>
</tr>
<tr>
<td>R</td>
<td>Ideal gas constant</td>
</tr>
<tr>
<td>$R^2$</td>
<td>Goodness-of-fit of linear regression</td>
</tr>
<tr>
<td>rac</td>
<td>Racemic mixture</td>
</tr>
</tbody>
</table>
rpm Rotations per minute
rR Resonance Raman Spectroscopy
RT-OMRP Reversible Termination Organometallic Mediated Radical Polymerization
S Spin state
Salen $bis$-(Schiff base) $bis$-(phenol)
SD Spin Density
SOMO Singly Occupied Molecular Orbital
$\sigma_{\text{para}}$ Hammett parameter (para substitution)
sq Single quantum
t Triplet (NMR)
T Temperature
t$_{1/2}$ Half life
TD-DFT Time Dependant Density Functional Theory
THF Tetrahydrofuran
TOF Time of flight
UV-Vis Ultraviolet-Visible spectroscopy
V Volts (Electrochemistry)
VAc Vinyl Acetate
VT Variable Temperature
vs. Versus
XPS X-ray Photoelectron Spectroscopy
Chapter 1. Introduction

1.1 Coordination Chemistry

Coordination chemistry is the study of chemical compounds resulting from the interaction between organic or inorganic functionalities with metal centers. Such functionalities surrounding the central metal atom are termed ligands, originating from the Latin verb *ligare*, to bind. The synthesis and characterization of such coordination compounds is vital to the understanding of the observed chemical and physical properties.

Coordination chemistry was pioneered by Alfred Werner, for which he was awarded the Nobel Prize in Chemistry in 1913.¹ Most notably, Werner studied several cobalt complexes with ammine and chloro ligands, all of which contained three chloride ions per cobalt ion, but exhibited different colors and physical properties (Figure 1.1). His observations led to the formulation that atoms (or molecules) can be bonded to a central atom in certain geometric patterns in the primary coordination sphere, while atoms in the outer (or secondary) coordination sphere balance the charge of the overall complex. He noted that the number of atoms in the primary coordination sphere, which he termed coordination number, often dictates the geometry around the central atom. For example, a coordination number of six, which he noted was especially common, typically results in an octahedral complex, where the coordinating ligands occupy the apices of an octahedron around the central atom. This became the basis of his well-known theory of coordination compounds.
Figure 1.1. Original and revised structures of cobalt complexes studied by Werner.

Coordination chemistry, and coordination compounds have had a profound impact on society. For instance, cis-platin, a platinum complex that has been intensely studied since its first reported synthesis in 1845 by Michele Peyrone (Figure 1.2).\textsuperscript{2-3} Unknown at the time, this complex would play a central role in the Nobel Prize winning work by Werner, where he, using his theory of coordination chemistry, correctly proposed its square-planar geometry. He was also able to distinguish between the cis and trans isomers, which are now known as cis-platin and trans-platin, respectively.\textsuperscript{1-2,4} Currently one of the most successful anticancer agents in the clinic, the biological activity of cis-platin is due to the inhibition of cellular division.\textsuperscript{5-8} The success of cis-platin has inspired much work towards the study of metal complexes as potential chemotherapeutic agents.\textsuperscript{9-13}

In the field of catalysis, Wilkinson’s catalyst, a rhodium complex named after Geoffrey Wilkinson, is used industrially to catalyze the hydrogenation of alkenes.\textsuperscript{14} More recently, Grubbs catalyst, a ruthenium complex named after Robert Grubbs (Nobel Prize, 2005), has shown exceptional utility in olefin metathesis.\textsuperscript{15-17} Stemming from these important discoveries, several generations of new catalysts based on these initial structures have been developed, primarily focusing on improving activity, chemoselectivity, and in some cases, stereoselectivity.\textsuperscript{18-25}
Metal complexes are often classified by the coordinating ligands, which may contain a variety of coordinating atoms and binding modes, the resultant geometry it adopts upon binding, and the oxidation state of the metal center. The oxidation state, which is an indication of the degree of oxidation of the metal, is central to the reactivity of the metal complex. The formal assignment of oxidation states assumes hypothetical charges of the metal center where all bonds are purely ionic, with both electrons in the metal-ligand bond assigned to the ligand such that the oxidation state will be the charge remaining on the metal center if all ligands were removed. While such formal oxidation states are often helpful for categorizing compounds, they are not measurable quantities since the majority of bonds carry some degree of covalency, or the sharing of electrons. To this end, Jørgensen and Wieghardt have promoted the idea of a spectroscopic (or physical) oxidation state, specifically to metal centers in coordination complexes, which are measurable and benchmarked using spectroscopic and crystallographic data.

1.2 Redox Active Ligands

Traditionally, redox processes (i.e. changes in oxidation state) of a metal complex are assigned to the metal center, implying that the metal ion is the source or sink for electrons transferred. However, this only holds true if the ligand is acting solely as a spectator and does not play a role in the redox process. Jørgensen was among the first to recognize that certain ligands are capable of undergoing redox changes, which he classified as “suspect” (or “non-innocent”) ligands. Such ligands are contradictory to the traditional dogma that ligands are unambiguously charged-defined such as H₂O, NH₃ or Cl⁻. Extending this concept, Ward and McCleverty coined the term “ambi-valent” ligands, and explained that non-innocent behavior of the ligand may also depend on the central metal ion. It is important to note that both terms, along with the term “redox
active ligands” have been used in the literature interchangeably, although one must be cognizant of the possibility of ligand ambi-valence even in cases where physical oxidation states have been established.35

In general, redox active ligands have energy levels that are accessible for change in their oxidation states in comparison to their redox inactive counterparts. In many cases, redox active ligands and the coordinated central metal ion have frontier molecular orbitals (Highest Occupied Molecular Orbitals, HOMO, and Lowest Unoccupied Molecular Orbitals, LUMO) of similar energies. As such, the locus of redox change for a metal complex with a redox active ligand is often challenging to assign. The relative energies of the frontier molecular orbitals dictates the locus of redox change: oxidation (i.e. loss of an electron) will occur from an occupied orbital highest in energy (Figure 1.3), while reduction (i.e. gain of an electron) will occur to an un-filled orbital lowest in energy (Figure 1.4). In certain cases the locus of redox change can be shifted by the solvent medium or even variation in temperature, demonstrating the similarities in energies of the two redox states.36-59

**Figure 1.3.** Possible oxidation processes for metal complexes with redox active ligands. Red dotted electron symbolizes electron lost in the oxidation.
This thesis will focus on assigning oxidation states of first row transition metal complexes involving redox active ligands. Specifically, the overall electronic structure of the complexes, which often dictates the associated reactivity, is of utmost interest. The elucidation of oxidation states and overall electronic structure of these complexes are often challenging, as numerous electronic structures are possible. As such, an array of experimental techniques, along with theoretical calculations has been employed to study the physical and chemical properties of these complexes, with the aim of utilizing them in oxidative catalysis.

1.3 Redox Active Ligands in Nature

In most cases, redox active ligands undergo single electron transfer to afford the corresponding radical species, an observation that has garnered significant attention.\(^{60}\) By extension, the study of metal-coordinated radicals has attracted much consideration in recent years, largely owing to their biological relevance.\(^{61-65}\) For instance, dioxygen (O\(_2\)), which has long been documented as a redox active ligand, is a substrate heavily associated with bioinorganic chemistry.\(^{66-70}\) O\(_2\) can undergo two sequential one-electron reduction reactions to form superoxide (O\(_2^–\)) and peroxide (O\(_2^{2–}\)) anions as intermediates, respectively, which under certain conditions ultimately leads to the cleavage of the O-O bond to generate water (Figure 1.5). This ambi-valence has
spurred much debate on the electronic description of oxygen transport proteins oxymyoglobin and oxyhemoglobin (Figure 1.5).\textsuperscript{71-75} The original formulation came from Pauling, who had described the binding of O\textsubscript{2} to the heme unit as a covalent interaction with a concurrent change in spin state from high spin Fe\textsuperscript{II} (\(S = 2\)) to low spin Fe\textsuperscript{II} (\(S = 0\)).\textsuperscript{72} This was later revised by Weiss, who postulated an electron transfer reaction from Fe\textsuperscript{II} to O\textsubscript{2} to afford an antiferromagnetically-coupled Fe\textsuperscript{III}(O\textsubscript{2}−•) species (Figure 1.5).\textsuperscript{73} The Weiss formulation was supported by other spectroscopic measurements as well as theoretical calculations.\textsuperscript{71,76-80} The ambi-valence of O\textsubscript{2} has also been observed in certain dicopper systems such as hemocyanin, where the two Cu\textsuperscript{I} centers can bind O\textsubscript{2} through two one-electron transfer reactions to afford a Cu\textsuperscript{II}-(\(\mu\)-O\textsubscript{2}) species (Figure 1.5). The O\textsubscript{2} in the bound state is formally a peroxide, demonstrated by numerous spectroscopic methods.\textsuperscript{81-84} Certain synthetic models developed can further activate this peroxide unit, ultimately splitting the O-O bond into two oxide (O\textsuperscript{2−}) moieties. While not observed in nature due to the high oxidation potential required to reach the Cu\textsuperscript{III} oxidation state, such oxide species are interesting synthetic models to consider due to their catalytic activity towards C-H activation.\textsuperscript{85-87}
Figure 1.5. $O_2$ as a redox active ligand, and examples of $O_2$ ambi-valence in bioinorganic chemistry, specifically in heme-based\cite{72,73} and Cu-based \cite{83} oxygen transport proteins.

The redox activity of NO, which can exist as the nitrosyl cation ($NO^+$), the nitric oxide radical ($NO$), or the nitroxyl anion ($NO^-$) through subsequent one-electron reductions\cite{92-94} (Figure 1.6), is believed to be responsible for its \textit{in vivo} activity.\cite{89-91} One well-known example is the “brown ring” ion $[Fe(NO)(H_2O)_5]^{2+}$, which can be described as $Fe^{I}/NO^+$, $Fe^{II}/NO^-$, or $Fe^{III}/NO^-$.\cite{95-96} A combination of electron
paramagnetic resonance and Mössbauer spectroscopies revealed that this ion is best described as a Fe\textsuperscript{III}/NO\textsuperscript{−} complex.\textsuperscript{96} With advances in crystallographic methods, structural information has also proven invaluable for analyzing bonding in NO-containing metal complexes. As the \(\pi\)-accepting ability decreases from NO\textsuperscript{+} to NO\textsuperscript{−}, the oxidation state of the NO fragment can be deduced from the bond distances and angle between the M-N-O atoms, where the smallest angle is expected for M-NO\textsuperscript{−} due to electron pair repulsion (Figure 1.6).\textsuperscript{94}

![Figure 1.6. NO as a redox active ligand, and its different bonding modes to metal ions.](image)

Metalloenzymes have been observed to exploit redox active ligands as a means to facilitate controlled multi-electron processes. In these cases, the ligand serves as an electron reservoir, where it takes advantage of its ambi-valence to accept or release an electron in synergy with the metal center during certain chemical transformations. One such example is the tyrosyl functional group, where both the phenolate (RO\textsuperscript{−}) and its one-electron oxidized phenoxyl (RO\textsuperscript{•}) moieties are implicated in the catalytic cycle of several metalloenzymes, such as Class I ribonucleotide reductase\textsuperscript{97-98}, prostaglandin endoperoxide synthase\textsuperscript{64,99}, photosystem II\textsuperscript{100-101}, cytochrome c oxidase\textsuperscript{102-103}, glyoxal oxidase\textsuperscript{104} and galactose oxidase.\textsuperscript{105-106} Of this series, the oxidase enzymes are especially interesting as they exhibit metal-ligand cooperativity to facilitate multi-electron redox processes. Galactose oxidase, in particular, is a mononuclear copper enzyme that catalyzes the two-electron oxidation of primary alcohols to aldehydes aerobically, with the concomitant reduction of O\textsubscript{2} to H\textsubscript{2}O\textsubscript{2} (Figure 1.7).\textsuperscript{106} The active site of galactose oxidase includes a Cu\textsuperscript{II} center coordinated by two histidine residues, one tyrosine and
one post-translationally modified tyrosine residue crosslinked with a neighboring cysteine moiety (Figure 1.8). This modification is critical in lowering the oxidation potential of modified tyrosine moiety, allowing for its oxidation under biological conditions (ca. 0.4 V vs. NHE). In its active state, the enzyme exists as a Cu$^{II}$-tyrosyl radical species. While copper typically undergoes single electron redox processes via the Cu$^{I}$/Cu$^{II}$ couple under biological conditions, the Cys modified tyrosyl moiety provides the second oxidizing equivalent required to promote catalytic alcohol oxidation.

*Figure 1.7.* Mechanism of action for Galactose Oxidase.
The hemoproteins are another example of redox active ligands in nature, specifically cytochrome P450. In general, the active site includes a heme component, a Fe$^{II}$-porphyrin unit, which is bound to the protein via an axial cysteine residue (Figure 1.9). In contrast to O$_2$ transport proteins, which are ligated by a histidine, the axial cysteine moiety has been shown to influence the pKa of the resultant Fe-oxo species, playing a critical role in the reactivity. Additionally, the sulfur atom from the cysteine moiety is hypothesized to play a role in stabilizing the electronic structure of the high valent Fe-oxo species via electron donation to the high valent Fe-oxo core. In the catalytic cycle (Figure 1.10), cytochrome P450 is activated upon a one-electron reduction, resulting in a cysteine bound Fe$^{II}$-heme unit, which then binds O$_2$ and reacts with two equivalents of H$^+$ and a further one-electron reduction to form a high valent species named Compound I. This highly reactive intermediate, which can hydroxylate unactivated C-H bonds with bond dissociation energies upwards of 100 kcal/mol, has been studied theoretically for many years, but definitive experimental evidence for the existence of this species has only been reported recently. The electronic structure of Compound I was ultimately confirmed experimentally to be an Fe$^{IV}$-oxo moiety coordinated by a ligand radical that is delocalized over the electron-rich porphyrin and the axially bound sulfur atom. Other possibilities, such as an Fe$^{V}$-oxo core
coordinated by diamagnetic ligands, have been explored theoretically, but little evidence supports this is as a viable electronic structure.\textsuperscript{79}

The discovery of the aforementioned metalloenzymes has inspired much work towards designing synthetic models containing ligand scaffolds capable of storing redox equivalents, and evaluation of their utility in multi-electron transformations.

\textbf{Figure 1.9.} Active site of cytochrome P450.\textsuperscript{112}
1.4 Synthetic Models Containing Redox Active Ligands

1.4.1 Dithiolenes

In the 1960s, Schrauzer and Mayweg discovered that the reaction of NiS₂ with diphenylacetylene resulted in the formation of a bis(dithiolene) complex (Figure 1.11). Based on chemical characterization, this complex was proposed as a square-planar structure through the chelation of two neutral dithiobenzil ligands, implying a Ni⁰ oxidation state. However, based on the geometry of the complex, a Ni^{II} oxidation state was assigned, suggesting that both dithiobenzil ligands are actually singly reduced to their dithiolene radical counterparts. This was further explored by Gray and co-workers, where bis(dithiolene) complexes of several dicationic metals (i.e. Ni^{II}, Pd^{II}, Pt^{II}, Co^{II}, Cu^{II}, Zn^{II}) were prepared (Figure 1.11). Depending on the substituent on the ligand backbone, the complexes can either contain two dianionic dithiolate ligands or two dithiolene radical anions chelating the metal ion (Figure 1.11). Concurrently, Davison and co-workers recognized such bis(dithiolene) complexes can undergo sequential one-
electron redox transformations. They were able to prepare each redox product independently, and found that these species exhibited very unusual electronic states (Figure 1.11).  

**Schrauzer and Mayweg:**

![Ni^{II}-(dithiolene)₂](image1)

**Gray and co-workers:**

![Ni^{II}-(dithiolene)₂](image2)

**Davison and co-workers:**

![Ni^{II}-(dithiolene)₂](image3)

**Figure 1.11.** Early examples of bis(dithiolene) complexes by Schrauzer and Mayweg, Gray and co-workers, and Davison and co-workers.

Since these seminal discoveries, there have been a large number of reports studying dithiolene containing complexes using both experimental and theoretical means. X-ray crystallography data collected at the time of their discovery was not of sufficient resolution to elucidate the oxidation state of the dithiolene ligand by bond length analysis. However, this has changed in recent years through significant technological advances in X-ray instrumentation (i.e. strength of source, multiple detectors) and data analysis. In addition, advances in sulfur K-edge X-ray absorption spectroscopy were vital in probing the oxidation state of the sulfur atoms, while the metal K- and L-edges were used in conjunction to assign the overall electronic structure of the complex.
Following these results, tris(dithiolene) complexes also garnered significant interest. Davison and co-workers reported the synthesis of a series of tris(dithiolene) complexes with a variety of metal centers (M = Cr, Mo, W, V, Figure 1.12), which they envisaged would undergo similar electron transfer reactions as the four-coordinate bis(dithiolene) complexes. Specifically, the tris(dithiolene) vanadium complex was capable of undergoing sequential reversible one-electron reductions resulting in multi-anionic species, affording an electron transfer series starting from the neutral complex. This paved the way for the spectroscopic investigation of their electronic structures, which confirmed that the redox processes were in fact ligand based.

![Figure 1.12. General structure of tris(dithiolene) complexes.](image)

**1.4.2 Dioxolenes (Quinones)**

Dioxolenes, the oxygen analogues of dithiolenes which are more commonly known as quinones, are ubiquitous components in biological systems which participate as electron acceptors in electron transport chains. Examples in nature include phylloquinone (Vitamin K) and plastoquinone which act as electron acceptors in light-driven reactions during photosynthesis in Photosystem I and II, respectively, while ubiquinone participates in aerobic cellular respiration (Figure 1.13).

![Figure 1.13. Examples of quinones in Nature.](image)

Quinones in nature generally exist with the oxygen donors para relative to one another. In the 1970s, extending on results from the study of dithiolene complexes,
reports of complexes of ortho-benzoquinones began to surface.\textsuperscript{133} Containing a similar 1,2-diheteroatom alkene motif to dithiolene, ortho-benzoquinones provide a favorable five-membered chelate site for a metal ion, while para-benzoquinones require additional donors for chelation, and the associated metal complexes are generally less stable.\textsuperscript{132,134} Perhaps the most studied family of redox active ligands, ortho-benzoquinones can exist in a variety of oxidation states, ranging from the dianionic catecholate, to the monoanionic radical semiquinone and finally to the neutral benzoquinones upon sequential one-electron oxidations (Figure 1.14).\textsuperscript{135-139}


One example in nature is catechol dioxygenase, which is an enzyme that features a non-heme iron center chelated by catecholate substrates. This enzyme can undergo intramolecular electron transfer between the metal center and catechol substrate to facilitate the binding and reductive activation of O\textsubscript{2}, ultimately promoting intra-diol cleavage (Figure 1.15).\textsuperscript{140-142} Another example in nature is the copper containing amine oxidases, which catalyze the oxidation of primary amines to aldehydes with the release of NH\textsubscript{3} and H\textsubscript{2}O\textsubscript{2} via an interaction with an electron rich topaquinone cofactor in a similar mechanism as catechol dioxygenase (Figure 1.15).\textsuperscript{143-144} These metalloenzymes are involved in the biosynthesis pathways of many biologically important molecules, such as catecholamines\textsuperscript{145-146} and melanin\textsuperscript{147-148}, and are also key to processes such as enzymatic oxidation\textsuperscript{143-144} and radical scavenging.\textsuperscript{149-150}

FIGURE 1.15. Iron containing catechol dioxygenase and copper containing amine oxidase.
Many dioxolene transition metal complexes have been prepared and studied. Much like their dithiolene counterparts, electronic structures involving a ligand radical that is delocalized over the ligand framework are commonly observed. Generally existing as the radical semiquinone or dianionic catecholate, the study of these complexes have revealed many fascinating features, such as their rich electrochemistry, radical magnetic coupling and even electron transfer equilibrium between metal and ligand in the solid and solution states. The latter, also known as valence tautomerism, is a concept that has been extended to many studies of metal-radical systems. In the seminal example by Pierpont and co-workers, a shift in charge distribution for a Co complex from Co$^{II}$-(semiquinone)$_2$ to Co$^{III}$-(semiquinone)(catecholate) was observed with a change in temperature (Figure 1.16). Since then, other factors that induce such a change in electronic structure, such as light or pressure, have been identified for analogous benzoquinone systems, highlighting the similarity in energy between the metal and ligand orbitals. Such tautomerism is of particular interest to the field of information storage, and for kinetic studies of electron transfer reactions.

![Figure 1.16. Valence tautomerism of a Co complex.](image)

The $N,O$ and $N,N$ derivatives of quinones, also known as iminoquinones and diimines, respectively, have also been extensively studied (Figure 1.17). These analogues display redox-active behavior akin to dioxolens, and have been highlighted in their utility as electron reservoirs for reactions such as C-C bond formation and halogen oxidation. These ligands represent critical examples for the use of redox-active ligands to promote multi-electron catalysis.
1.4.3 Bipyridines and other α-Diimines

Discovered towards the end of the nineteenth century\textsuperscript{164}, bipyridine and its derivatives are one of the oldest ligand families, and the coordination chemistry has been extensively investigated with a plethora of different metals.\textsuperscript{165} In particular, complexes containing the bipyridine ligand have been used for assembling supramolecular structures\textsuperscript{166-168}, and luminescent devices for photonics and optoelectronic applications.\textsuperscript{169-172} Over the course of these studies, several isomers of bipyridine were identified; however only the 2,2′ derivative has been recognized as a redox active ligand. Importantly, this isomer of bipyridine also contains the 1,2-diheteroatom alkene motif that contributes to the redox activity of other organic moieties such as the dithiolene and dioxolene ligands.\textsuperscript{173-175} The sequential one-electron reduction of the bipyridine framework leads to a semiquinone-like radical species and then a catecholate-like dianionic species, respectively, exhibiting similar electronic structures to those observed for dithiolene and dioxolene (Figure 1.18). Wieghardt and co-workers have demonstrated that \textit{tris}-2,2′-bipyridine complexes of Y\textsuperscript{174-175}, Ti\textsuperscript{176}, V\textsuperscript{176-177}, Cr\textsuperscript{178}, Mo\textsuperscript{176}, Mn\textsuperscript{179}, Fe\textsuperscript{180} and Ru\textsuperscript{180} can undergo ligand based reduction to form ligand radical species. Similarly, 1,4-diazabutadiene, a non-aromatic analogue of bipyridine and the simplest α-diimine, has also been studied extensively as a redox active ligand, with electronic structure akin to its bipyridine counterparts (Figure 1.18).\textsuperscript{181-185} The electronic structures of these isolated products have been investigated by an arsenal of experimental methods, ranging from solution state measurements such as resonance Raman, electron paramagnetic resonance, $^1$H NMR spectroscopies, to solid state magnetic susceptibility and X-ray crystallography. In certain cases, isotope specific techniques such as X-ray absorption or Mössbauer spectroscopy have been critical in the assignment of the electronic structure.\textsuperscript{178,180} Finally, theoretical methods
such as density functional theory have also played an important role in the assignment of electronic structure.\textsuperscript{178}

\[
\begin{align*}
\text{Dotted: } & 2,2'\text{-bipyridine} \\
\text{Solid: } & 1,4\text{-diazabutadiene}
\end{align*}
\]

**Figure 1.18.** Bipyridine ligand, and various oxidation states of 2,2'-bipyridine and 1,4-diazabutadiene.

\(\alpha\)-Iminopyridines, a combination of bipyridine and 1,4-diazabutadiene, have also received much attention. Initially utilized as a neutral ligand for olefin polymerization catalysts\textsuperscript{186-187}, there has been increasing recognition that this ligand scaffold is also redox active similar to its bipyridine counterpart. For example, the Cr\textsuperscript{188-189}, Mn\textsuperscript{188}, Fe\textsuperscript{188}, Co\textsuperscript{188,190}, Ni\textsuperscript{188}, and Zn\textsuperscript{188,191} complexes of such \(\alpha\)-iminopyridine ligands with different oxidation states have been prepared and studied with the same spectroscopic techniques discussed above for the bipyridine complexes. Notably, the isolation of the Co complex containing a neutral, monoanionic and dianionic \(\alpha\)-iminopyridine ligand allowed for high resolution X-ray crystallographic analysis, which revealed significant differences in the bonding parameters (Figure 1.19).\textsuperscript{188,190} This was further observed in a structurally similar Cr-imido complex, where the oxidation results in similar changes in the bonding of the ligand scaffold.\textsuperscript{188-189}

\[
\begin{align*}
\text{Figure 1.19.} & \text{ Different oxidation states and corresponding bonding distances (in Å) of } \alpha\text{-iminopyridines.} \\
\end{align*}
\]

Addition of a second imino functionality to the pyridine of \(\alpha\)-iminopyridines results in bis(imino)pyridines, which undergo sequential one-electron reductions in a similar manner to \(\alpha\)-iminopyridines (Figure 1.20).\textsuperscript{192-203} Similar changes in the metrical
parameters were observed, highlighting its similarity to the \( \alpha \)-iminopyridines. Along the same lines, the addition of a pyridine moiety to bipyridine affords terpyridines\(^{204} \), which exhibits similar electrochemical behavior to the \( \text{bis(imo)} \text{pyridines} \) (Figure 1.20).\(^{176,179-180} \)

Other examples of nitrogen based redox active ligands include benzoquinone-derived \textit{ortho}-phenylenediamine\(^{205-207} \) and diaminophenanthrenes\(^{208} \), porphyrin-derived dipyrrromethenes\(^{209-210} \) and phthalocyanines.\(^{211-216} \)

**Figure 1.20.** Other nitrogen containing redox active ligands.

### 1.4.4 Salens and other Phenol Containing Ligands

Inspired by the active site and reactivity of Galactose oxidase, as well as the preparation of the first stable phenoxy radical transition metal complex by Wieghardt and co-workers\(^{217} \) (Figure 1.21), there has been much interest in phenolate containing metal complexes, and their one-electron oxidized phenoxy radical complexes.\(^{65,218-220} \)

Stemming from these discoveries, many small molecule metal-phenoxy systems employing different metals and ligand frameworks have been studied. Ligands such as the bidentate \textit{ortho}-aminophenol\(^{221} \), \textit{ortho}-thiophenol, tridentate \( \text{bis(phenol)amines} \)\(^{221-229} \),

![Diagrams of ligands](image)
bis(phenol)thioethers\textsuperscript{226,230-232}, bis(phenol)selenoethers\textsuperscript{226,230-233}, tetradequate bis(phenol)pyridylamine\textsuperscript{44,234-236}, bispyridylaminephenol\textsuperscript{44,236-239}, bis(phenol)-ortho-phenylenediamine\textsuperscript{240} and multideadate 1,4,7-triazacyclononane derivatives\textsuperscript{241-246} have attracted the most interest (Figure 1.20).

![Bidentate and Tridentate Bis(phenol) Ligands](image)

**Figure 1.21.** Phenol containing redox active ligands.

Salen ligands, or bis-Schiff-base bis-phenol ligands, were first reported in the late nineteenth century.\textsuperscript{247} Since then, they have been used extensively in coordination chemistry and catalysis due to their modular synthesis and ability to bind a variety of transition metal ions in different oxidation states.\textsuperscript{248-250} Typically synthesized by the condensation of two equivalents of salicylaldehyde and one equivalent of diamine, an array of symmetric salen ligands can be prepared with various functional groups on the phenol moieties and with various diamine linkers (Figure 1.22). The imino moiety can also be reduced to afford the corresponding amino-phenol ligands, which are aptly named “reduced salens” (Figure 1.22).\textsuperscript{51,251-253} Half reduced salens, where only one
imino functionality has been reduced, have also been identified. Finally, Campbell and Nguyen developed synthetic methodologies to synthesize asymmetric salens\textsuperscript{255}, which allows for near endless permutations of ligands that can be studied (Figure 1.22). The terms symmetric and asymmetric usually refers to the substitution pattern on the aromatic phenol moiety, and does not represent molecular point group assignments.

**Figure 1.22.** Synthesis of Salen ligands and analogues.

Oxidation of these phenolate containing metal complexes often results in ligand based oxidation to afford the corresponding phenoxyl radical, where in certain cases, a characteristic quinoidal distribution in the aromatic phenoxyl moiety can be observed by high resolution crystallographic measurements. Differences in the metrical parameters of phenolate vs. phenoxyl was observed in the first structurally characterized phenoxyl radical complex by Wieghardt and co-workers, a chromium complex coordinated by two phenolates and one phenoxyl moiety (Figure 1.23).\textsuperscript{246} The Cr-O bond distance of the phenoxyl radical was elongated by 0.02 Å in comparison to the phenolates, consistent with a decreased donating ability of the phenoxyl moiety. In addition, the C-O bond distance of the phenoxyl radical was shortened by 0.12 Å, which, in combination with the
shortening of the conjugated C-C bonds, affords the characteristic quinoidal distribution pattern (Figure 1.23). Similar changes in metrical parameters upon oxidation have also been observed for several salen complexes$^{43,53-54,56,256-257}$, although caution must be taken in this analysis as solid state packing effects can also play a major role in bond length changes. One crucial aspect in ligand design is phenolate substitution at the ortho and para positions, which ensures the stability of the resultant phenoxy radical complexes upon oxidation. The radical coupling of such phenoxy radical species has been observed even at temperatures as low as -125 °C.$^{258}$ In addition to crystallography, X-ray absorption, near-IR, electron paramagnetic resonance, electrochemistry and resonance Raman spectroscopies, as well as density functional theory calculations have all played critical roles in the assignment of the locus of oxidation as well as the overall electronic structure of the complexes mentioned above.$^{207,254}$

![Figure 1.23. Phenolate vs. phenoxy ligand bond distances (in Å).](image)

### 1.5 Redox Active Ligands in Catalysis

Bond-making and breaking reactions are generally catalyzed by precious metals, as they typically undergo controlled two-electron redox changes (i.e. Pd$^{0}$ to Pd$^{II}$ to Pd$^{IV}$). However, due to the continual rise in prices for such metals, research in base metal alternatives (i.e. first row transition metals) has attracted increasing interest. These base metals, while earth abundant and thus less costly than their precious metal counterparts, are limited by their propensity to undergo one-electron redox changes (i.e. Ni$I$ to Ni$^{III}$ to Ni$^{III}$). While successive one-electron transfer can afford the same two-electron reactivity,
one must be aware of undesired side reactions arising from the first electron transfer
reaction. To this end, Chirik and Wieghardt have proposed the use of redox active
ligands in conjunction with base metals, in which one-electron redox changes will occur
on both the metal and ligand for an overall two-electron change.\textsuperscript{202} Since that time,
there have been many extensive reviews and forums highlighting the use of redox active
ligands in catalysis, truly signifying the growth of this field of research.\textsuperscript{259-263} It is
important to note that while synthetic model systems invoking ligand radicals for
stoichiometric reactivity have been shown, such ligand participation in catalysis has
been lacking outside of a few galactose oxidase model systems.\textsuperscript{218-219} This may be due
to difficulties in the isolation and characterization of a highly reactive ligand radical
species formed during catalysis, or even the lack of such a ligand radical species. As
such, the focus of this thesis will be on the investigation of ligand radical formation and
their resultant electronic structures using experimental and theoretical methods, with the
ultimate goal being to reveal their unique spectroscopic markers for the investigation of
catalytic intermediates.

1.6 Thesis Synopsis

In this thesis several projects involving the design and characterization of
complexes containing redox active ligands are discussed. Focusing on phenolate
ligands, the properties and electronic structure of their corresponding metal complexes
were studied by a series of experimental (i.e. electrochemistry, UV-Vis-NIR, EPR, rR
etc.) and theoretical (DFT) methods. These studies have shed much light on the
electronic structure of several phenolate containing complexes, with the ultimate goal of
correlating the electronic structure with catalytic properties. This thesis provides a solid
foundation for evaluating the electronic structure of phenolate containing complexes,
which is key in designing effective catalysts, as well as a starting point for using such
complexes to catalyze the oxidation of more challenging substrates.

In Chapters 2 and 3, electron rich and deficient nickel-salen complexes are
discussed, respectively. The oxidation potentials of the ligand were predictably
decreased as the electron donating ability of the para-ring substituents was increased
(NMe\textsubscript{2} > OMe > tBu > CF\textsubscript{3}). Remarkably, the oxidation of these geometrically-symmetric
complexes afforded an asymmetric electronic structure in a number of cases, in which
the ligand radical was localized on one phenolate rather than delocalized across the
ligand framework. This difference in electronic structure was found to be dependent on
the electron donating ability of the substituents; a delocalized ligand radical was
observed for electron withdrawing substituents and a localized ligand radical for strongly
donating substituents. This observation suggests that para-ring substituents can be
used to tune the electronic structure (metal vs. ligand based, localized vs. delocalized
radical character) of metallosalen complexes.

The corresponding cobalt complexes of the aforementioned salen ligands were
prepared and discussed in Chapter 4, with the aim of evaluating whether ligand
electronic tuning through para-ring substitution can be applied to the Co metal center.
Indeed, the electronic properties of the metal center were also significantly affected by
para-ring substitution, evidenced by a shift in the oxidation potential of the metal center.
These cobalt-salen complexes were tested in organometallic radical mediated
polymerizations, with the most electron rich complexes displaying the highest conversion
rates.

Two novel iron complexes containing one or two redox active phenolate
fragments were prepared and are discussed in Chapter 5. These iron complexes
feature a chiral bipyrrolidine backbone; ligands with this backbone are known to bind
metals diastereospecifically owing to increased backbone rigidity, which is critical to
stereospecificity in catalysis. A symmetric (two phenol) ligand was prepared by reported
methods, and a novel route to synthesize an asymmetric ligand (one phenol and one
pyridine) from symmetric starting materials was established. These neutral iron-
complexes were both found to be high spin ($S = 5/2$), and can undergo ligand-based
oxidation to form an antiferromagnetically coupled ($S_{\text{total}} = 2$) species.

1.7 References


   (4), 250-256.


Chapter 2. Ligand Radical Localization of Symmetric One-Electron Oxidized Nickel Salen Complexes

Adapted from: Chiang, L.¹, Kochem, A.², Jarjayes, O.², Dunn, T. J.¹, Vezin, H.³, Sakaguchi, M.⁴, Ogura, T.⁴, Orio, M.³, Shimazaki, Y.⁵, Thomas, F.², and Storr, T.¹, Chem. Eur. J., 2012, 18, 14117-14127.

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LC performed the synthesis, chemical oxidation, electrochemistry, UV-Vis-NIR, continuous wave EPR experiments and theoretical calculations. YS collected the rR data. FT performed the pulsed EPR experiments.

2.1 Introduction

Investigations of nickel complexes involving salen ligands demonstrate that two electronic structures, either \([\text{Ni}^{II}(\text{Salen})]^{+}\) or \([\text{Ni}^{III}(\text{Salen})]^{+}\), can be obtained upon one-electron oxidation.¹⁻²⁶ Parameters such as the coordinating ability of the solvent, the relative electron-donating properties of the phenolate substituent, and temperature have
all been found to influence the locus of oxidation, demonstrating the similarity in energy between the frontier molecular orbitals of the metal and ligand. In this Chapter, Ni-salen complexes with a variety of para-ring substituents were investigated (Figure 2.1), and their one-electron oxidized counterparts was prepared by chemical oxidation. The ortho and para positions of the aromatic ring on the salen ligand scaffold are commonly derivatized to prevent decomposition, as a significant amount of spin density is harboured by those positions upon oxidation. The resultant electronic structures were correlated with the donating ability of the para-ring substituents through a series of experimental and theoretical methods. This strategic substitution was applied to a Cu-salen complex bearing a para-thiolate substituent, mimicking the active site of the Cu-containing metalloenzyme galactose oxidase.

Figure 2.1. Structures of NiII-salen complexes (Ni(Sal)R).

Recent X-ray crystal structure determinations of one-electron oxidized NiII-salen radical complexes provide significant insight into ligand radical delocalization. For example, \([\text{Ni(Sal)}^\text{Bu}]^{+}\) exhibits a symmetric structure with similar metrical parameters in both aromatic rings in the solid state, while the coordination sphere was contracted when compared to its neutral precursor. On the other hand, \([\text{Ni(Sal)}^{\text{OMe}}]^{{+}}\) displays an asymmetric structure in the solid state, in which one aromatic ring exhibits structural features of a phenolate while the second exhibits the quinoidal distribution of bond lengths expected for a phenoxy radical. In addition, the coordination sphere was found to be strongly asymmetric, with a long Ni-O bond ascribed to the phenoxy moiety, a pattern that was also observed for a Cr-phenoxyl radical complex by Wieghardt and co-workers. In combination, these results indicate that the radical SOMO is fully
delocalized in \([\text{Ni(Sal)}^{\text{Bu}}]^{+}\), while it is at least partially localized on one of the two phenolate rings in \([\text{Ni(Sal)}^{\text{OMe}}]^{+}\).

The overall electronic structure of such mixed-valence species, where the locus of oxidation is delocalized over several redox active fragments, can be studied through analyzing the shape and intensity of their intervalence charge transfer bands (IVCT) by electronic spectroscopy.\(^{30}\) An IVCT band generally corresponds to electronic transitions between a coupled ground state to the coupled excited state, as described by the Hush model (Figure 2.2). Two ground states, modelled by harmonic functions, are placed along the electron transfer coordinate \(x\) where the surface minima are at \(x = 0\) and \(1\), which represents the localization of the unpaired electron completely on one redox-active moiety. The two ground states can be coupled, resulting in two new energy surfaces: A low energy surface (coupled ground state) with minima positioned near \(x = 0\) and \(1\) separated by a thermal barrier at \(x = 0.5\), and a high energy surface (coupled excited state) with a single minimum at \(x = 0.5\). The observed IVCT arises from the excitation from the coupled ground state to excited state.

One of the first examples of a mixed-valence complex was the Creutz-Taube ion, a diruthenium complex bridged by an organic pyrazine unit with the formula \([(\text{NH}_3)_5\text{Ru}(\mu-\text{pyz})(\text{Ru(NH}_3)_5)]^{5+}\) (Figure 2.3).\(^{31}\) Numerous examples of model complexes

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**Figure 2.2.** Hush model of an IVCT, where the two harmonic ground states (dotted lines) are coupled to form low and high energy surfaces (solid lines). \(\lambda\) signifies the excitation wavelength of the IVCT, \(x\) signifies the reaction coordinate. See text for further discussion.
in the form of ligand-bridged dinuclear polypyridyl complexes have been examined with the aim to study intramolecular electron transfer between the metal centers. However, one fundamental issue arising from the studies of such mixed-valence complexes is the degree of electronic coupling mediated by an organic linker, which is manifested in overall electronic structure of such compounds. To this end, Robin and Day established a classification system for localized (Class I, where the valences cannot easily interconvert, and Class II, where interconversion may occur under thermal or photochemical activation) and delocalized (Class III) mixed-valence species, and Hush provided a theoretical model for such intervalence charge transfer. In the case of the Creutz-Taube ion, formal charges of Ru$^{II}$ and Ru$^{III}$ can be assigned to the metal centers. However, this ion has been characterized as a Class III mixed-valence species by crystallographic and theoretical methods, suggesting that the physical oxidation states are more along the lines of 2.5+ on each metal center.

![Structure of the Creutz-Taube ion.](image)

While the Robin-Day classification system was originally developed to analyze the electronic coupling in metal-centered mixed valence systems, this work has more recently been extended to ligand-based mixed-valence systems in which the electronic coupling is mediated by a metal center. For example, complexes of the salen ligand, as discussed in Chapter 1, contain two redox active phenolate moieties chelated to a metal center. It is possible that the oxidation of such complexes can afford a localized (Class II, oxidation on one phenolate) or delocalized (Class III, oxidation spread out over the entire ligand scaffold) electronic structure. Near-infrared (NIR) spectroscopy has been especially useful in studying the electronic structure of such oxidized species, as the IVCT band is often observed at low energies.

The NIR band for $[\text{Ni(Sal)}^{\text{Bu}}]^{2+}$ provided further support for classification of this species as a Robin-Day Class III (fully delocalized) mixed-valence complex. Fujii and co-workers have reported the NIR spectrum of $[\text{Ni(Sal)}^{\text{OMe}}]^{2+}$, which displays a NIR band...
of lower intensity in comparison to [Ni(Sal)\textsuperscript{tBu}]\textsuperscript{2+}.\textsuperscript{39} This observation is consistent with partial ligand radical localization in [Ni(Sal)\textsuperscript{OMe}]\textsuperscript{2+} as suggested from the solid state structure.\textsuperscript{28} An initial expectation was that the enhanced electron donating ability of the para-OMe ring substituents would increase the ligand character of the SOMO in [Ni(Sal)\textsuperscript{OMe}]\textsuperscript{2+} leading to enhanced radical delocalization in comparison to [Ni(Sal)\textsuperscript{tBu}]\textsuperscript{2+}. The reported experimental results suggest exactly the opposite, leading to this investigation of the series of complexes [Ni(Sal)\textsuperscript{R}]\textsuperscript{2+} by both experimental and theoretical methods to better understand the electronic structure and coupling between the redox active phenolates. In addition to the previously reported Ni-salen complexes, Ni(Sal)\textsuperscript{NMe\textsubscript{2}}, which contains strongly electron-donating para-NMe\textsubscript{2} ring substituents, was included to provide a series of compounds with a range of electron donating abilities (NMe\textsubscript{2} > OMe > tBu).

2.2 Experimental

2.2.1 Materials

All chemicals used were of the highest grade available and were further purified whenever necessary.\textsuperscript{40} Literature methods were followed to prepare 3-tert-butyl-5-dimethylamino-2-hydroxy-benzaldehyde,\textsuperscript{41} (N,N'-bis(3,5-di-tert-butylsalicylidene))-trans-1,2-cyclohexanediamine Nickel (Ni(Sal)\textsuperscript{tBu}),\textsuperscript{42} and (N,N'-bis(3-tert-butyl-5-methoxy-salicylidene))-trans-1,2-cyclohexanediamine Nickel (Ni(Sal)\textsuperscript{OMe}).\textsuperscript{28}

2.2.2 Instrumentation

2.2.2.1 General

\textsuperscript{1}H NMR spectra were recorded on Bruker AV-400 or AV-500 instruments. Mass spectra (positive ion) were obtained on an Agilent 6210 TOF ESI-MS instrument. Electronic spectra were obtained on a Cary 5000 spectrophotometer with a custom-designed immersible fiber-optic quartz probe with variable path length (1 and 10 mm; Hellma, Inc.). Constant temperatures were maintained by a dry ice/acetone bath. Solvent contraction was accounted for in all variable temperature studies. Cyclic
voltammetry (CV) was performed on a PAR-263A potentiometer, equipped with an Ag wire reference electrode, a platinum disk working electrode and a Pt counter electrode with $^t\text{Bu}_4\text{NClO}_4$ (0.1 M) solutions in CH$_2$Cl$_2$. Decamethylferrocene was used as an internal standard.\(^{43}\)

2.2.2.2 Continuous Wave EPR

All EPR spectra were collected using a Bruker EMXplus spectrometer operating with a premiumX X-band (~9.5 GHz) microwave bridge. Low temperature measurements of frozen solutions used a Bruker helium temperature-control system and a continuous flow cryostat. Samples for X-band measurements were placed in 4 mm outer-diameter sample tubes with sample volumes of ~300 μL. Spectra at 298 K were collected in capillary tubes, which were placed inside a standard EPR tube. EPR spectra were simulated with EasySpin 3.1.7 software.\(^{44}\)

2.2.2.3 Pulsed EPR

Pulsed EPR experiments were carried out at X-band (9.64 GHz) with a Bruker ELEXSYS E580 FT spectrometer. The spectrometer is equipped with an Oxford Helium flow cryostat for measurements between 4 K and room temperature. A spin echo is generated by a series of $\pi/2$ and $\pi$ microwave pulses ($\pi/2$ and $\pi$ represent the rotation angles of electron magnetization), with controlled time delays between pulses. By variation of these time delays, the echo intensity exhibits modulations at the frequencies of the hyperfine interactions. The pulse sequence $\pi/2$-$\tau$-$\pi/2$-$t_1$-$\pi$-$t_2$-$\pi/2$-$\tau$-echo (HYperfine Sublevel CORrelation Spectroscopy, HYSCORE) was used, whereby an echo is generated at time $\tau$ after the last $\pi/2$ pulse, with $\tau$ representing the delay between the first two $\pi/2$ pulses. The echo intensity is measured at each $t_1$ and $t_2$ value, and is varied stepwise at constant $\tau$. This two-dimensional set of echoes gives, after Fourier transformation along $t_1$ and $t_2$, a two-dimensional HYSCORE spectrum.\(^{45}\) The lengths of the $\pi/2$ and $\pi$ pulses were 16 and 32 ns, respectively, and a delay of $\tau = 128$ ns between the first two $\pi/2$ pulses gave the best sensitivity and resolution for the detection of $^1\text{H}$, $^{14}\text{N}$, and $^{19}\text{F}$ peaks, with no blind-spot effect. HYSCORE spectra were recorded with $256 \times 256$ data points for both $t_1$ and $t_2$ time domains. Prior to Fourier
transformation of the HYSCORE data, the background decay was removed using a polynomial fit and apodized with a Hamming function.

### 2.2.2.4 Resonance Raman

Resonance Raman spectra were obtained on a MC-100DG spectrometer (Ritsu Oyo Kogaku) with a Beamlok Kr ion laser (Spectra-Physics) for 413.1 nm excitation and a GLG3200 Ar ion laser (NEC) for 457.9 nm excitation, a holographic supernoch filter (Kaiser Optical Systems) and Symphony CCD detector (HORIBA Jobin Yvon) cooled with liquid N₂. Spectra were collected on solvated samples in spinning cells (0.5 cm diameter, 330 rpm) at 213 K, 135° back scattering geometry, and 5 minute data accumulation. Peak frequencies were calibrated relative to indene standards (accurate to ± 1 cm⁻¹).

### 2.2.3 Oxidation Protocols

Under an inert atmosphere, a solution of \textbf{Ni(Sal)}^R (0.011 mmol) in CH₂Cl₂ (1 mL) was added 100 µL of a solution of AgSbF₆ in CH₂Cl₂ (3.7 mg in 1 mL CH₂Cl₂, 0.011 mmol). This solution was stirred for 30 minutes at room temperature until a silver mirror was formed, and then was filtered through Celite. The resultant solution of \([\textbf{Ni(Sal)}^R]^*\) was used directly in further studies.

### 2.2.4 Calculations

Geometry optimizations were performed using the Gaussian 09 program (Revision A.02), the CAM-B3LYP functional, and the 6-31G(d) basis set on all atoms. A symmetric structure was used as a starting point for all geometry optimizations. Frequency calculations at the same level of theory confirmed that the optimized structures were located at a minimum on the potential energy surface. Single point calculations were performed using the CAM-B3LYP functional and the TZVP basis set of Ahlrichs on all atoms. The intensities of the 30 lowest-energy electronic transitions were calculated by TD-DFT at the CAM-B3LYP/TZVP level. The above calculations were also completed using the B3LYP functional for comparison.
AOMix$^{54-56}$ was used for determining atomic orbital compositions employing Mulliken Population Analysis.

### 2.2.5 Synthesis

$(N,N’\text{-bis}(3\text{-}\text{tert}\text{-butyl-5-dimethylamino})\text{salicylidene})\text{-trans-1,2-cyclohexanediamine} (H_2(\text{Sal})^{\text{NMe}_2})$:

To a solution of trans-1,2-cyclohexanediamine (120 mg, 1.05 mmol) dissolved in EtOH (10 mL) was added 3-\text{tert}-butyl-5-dimethylamino-2-hydroxybenzaldehyde (465 mg, 2.10 mmol) in EtOH (30 mL), and the solution was heated to reflux overnight. After cooling at room temperature, the reaction mixture was concentrated in vacuo, and the crude material was purified by column chromatography in 50:1 CH$_2$Cl$_2$:MeOH to yield a light yellow powder. Yield: 421 mg (77%). $^1$H NMR (CDCl$_3$): $\delta = 8.24$ (s, 2H), 6.88 (d, $^4$J = 2.9 Hz, 2H), 6.42 (d, $^4$J = 2.9 Hz, 2H), 3.31 3.27 (m, 2H), 2.75 (s, 12H), 1.89–1.76 (m, 10H), 1.40 (s, 18H). MS (ESI): m/z (%): 521.5 (100) $[\text{H}_2(\text{Sal})^{\text{NMe}_2} + \text{H}]^+$. Elemental Analysis: calculated for C$_{32}$H$_{48}$N$_4$O$_2$: Calcd. C 73.81, H 9.29, N 10.76. Found: C 73.68, H 9.39, N 10.67.
(N,N'-bis(3-tert-butyl-5-dimethylaminosalicylidene))-trans-1,2-cyclohexanediamine Nickel (Ni(Sal)<sub>NMe<sub>2</sub></sub>):

To a solution of H<sub>2</sub>(Sal)<sub>NMe<sub>2</sub></sub> (110 mg, 0.21 mmol) in EtOH (10 mL), was added Ni(OAc)<sub>2</sub>•4H<sub>2</sub>O (53 mg, 0.21 mmol) in EtOH (5 mL) and a few drops of NEt<sub>3</sub>. The resulting solution was heated at reflux for 2 hours during which time a brown precipitate appeared, which was collected by filtration and washed with cold EtOH. Yield: 89 mg (73%). MS (ESI): m/z (%): 577.4 (100) [Ni(Sal)<sub>NMe<sub>2</sub></sub> + H]<sup>+</sup>. Elemental Analysis: calculated for C<sub>32</sub>H<sub>46</sub>N<sub>4</sub>NiO<sub>2</sub>: Calcd. C 66.56, H 8.03, N 9.70. Found: C 66.62, H 7.89, N 9.76.

2.3 Results and Discussion

2.3.1 Synthesis

The ligand H<sub>2</sub>(Sal)<sub>NMe<sub>2</sub></sub> was synthesized by condensation of trans-1,2-cyclohexanediamine in the presence of two equivalents of 3-tert-butyl-5-dimethylamino-2-hydroxybenzaldehyde. Metallation of H<sub>2</sub>(Sal)<sub>NMe<sub>2</sub></sub> with Ni(OAc)<sub>2</sub>•4H<sub>2</sub>O in the presence of two equivalents of NEt<sub>3</sub> affords Ni(Sal)<sub>NMe<sub>2</sub></sub> (Scheme 2.1). The solid state structures of Ni(Sal)<sub>TBu</sub> and Ni(Sal)<sub>OMe</sub> have been reported and both exhibit an essentially symmetric N<sub>2</sub>O<sub>2</sub> coordination sphere (Table 2.2).<sup>14,28</sup> X-ray quality crystals of Ni(Sal)<sub>NMe<sub>2</sub></sub> could not be isolated for analysis.
Scheme 2.1. Synthesis of \( \text{H}_2(\text{Sal})^{\text{NMe}_2} \) and \( \text{Ni}(\text{Sal})^{\text{NMe}_2} \).

Reaction Conditions: (i) EtOH, 80ºC; (ii) Ni(OAc)\(_2\)•4H\(_2\)O, 2 eq. NEt\(_3\), EtOH, 80ºC.

2.3.2 Electrochemistry

Redox processes for \( \text{Ni}(\text{Sal})^R \) were probed by cyclic voltammetry (CV) in CH\(_2\)Cl\(_2\) by using tetra-\( n \)-butylammonium perchlorate (\( ^n\text{Bu}_4\text{NClO}_4 \)) as the supporting electrolyte (Figure 2.4). The redox potentials versus Fc\(^+/\text{Fc} \) are reported in Table 2.1. Two quasi-reversible one-electron oxidation waves are observed for all three complexes, which are assigned to ligand-based oxidations to afford the corresponding phenoxyl radical species.\(^3\text{,7-8} \) The trend in the oxidation potentials for the three derivatives are in line with the relative electron donating ability of the \( \text{para} \)-substituents (\( \text{NMe}_2 > \text{OMe} > \text{tBu} \)) on each of the phenolate moieties.
Figure 2.4. Cyclic Voltammograms of: (a) Ni(Sal)$_{tBu}$; (b) Ni(Sal)$_{OMe}$ and (c) Ni(Sal)$_{NMe2}$ in CH$_2$Cl$_2$ at 233 K.
Conditions: 1 mM complex, 0.1 M $^{n}$Bu$_4$NClO$_4$, scan rate 100 mV s$^{-1}$.

Table 2.1. Redox Potentials for Ni(Sal)$^R$ versus Fc$^+/Fc^a$.43

<table>
<thead>
<tr>
<th>Complex</th>
<th>$E_{1/2}^1$ (V)</th>
<th>$E_{1/2}^2$ (V)</th>
<th>$\Delta E_{1/2}$ (V)</th>
<th>$K_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(Sal)$_{tBu}$</td>
<td>0.37 (0.14)</td>
<td>0.85 (0.14)</td>
<td>0.48</td>
<td>2.4 x 10$^{10}$</td>
</tr>
<tr>
<td>Ni(Sal)$_{OMe}$</td>
<td>0.22 (0.14)</td>
<td>0.59 (0.14)</td>
<td>0.38</td>
<td>1.7 x 10$^8$</td>
</tr>
<tr>
<td>Ni(Sal)$_{NMe2}$</td>
<td>-0.24 (0.14)</td>
<td>-0.08 (0.14)</td>
<td>0.16</td>
<td>2.9 x 10$^3$</td>
</tr>
</tbody>
</table>

$^a$ Peak-to-peak differences in brackets ($|E_{pa} - E_{pc}|$ in V). Peak-to-peak difference for the Fc$^+/Fc$ couple at 233 K is ca. 0.13 V.
The difference between the first and second oxidation potentials ($\Delta E_{1/2}$), which can provide information on the degree of electronic coupling between the two redox-active phenolates in $[\text{Ni(Sal)}^R]^{$**}$ and the extent of electronic delocalization, are shown in Table 2.1. In the absence of electronic coupling a symmetric complex with two equivalent redox-active components will exhibit two redox processes separated by a theoretical value of $\Delta E_{1/2} = \frac{RT}{F} \ln 4$ (i.e. $\Delta E_{1/2} (233 \text{ K}) = 28 \text{ mV}$), which is not usually observed experimentally. The electronic structure of $[\text{Ni(Sal)}^R]^{$**}$ can be quantified by its comproportionation constant ($K_c$), which is a measure of the degree of delocalization, and can be calculated by Equations 1-3. This equilibrium constant takes into account the relative stability between the one-electron oxidized species versus the neutral and two-electron oxidized species (Eq. 1). A larger $K_c$ value is obtained as the stability of the one-electron oxidized species is increased via delocalization (Eq. 3).

$$\text{[ML]} + \text{[ML]}^{**} \leftrightarrow 2\text{[ML]}^*$$  \hspace{1cm} (1)

$$K_c = \frac{[\text{ML}^*]^2}{[\text{ML}][\text{ML}^{**}]}$$  \hspace{1cm} (2)

$$K_c = \exp\left(\frac{\Delta E_{1/2}F}{RT}\right)$$  \hspace{1cm} (3)

The values of $\Delta E_{1/2}$ and $K_c$ for $\text{Ni(Sal)}^\text{tBu}$ and $\text{Ni(Sal)}^\text{OMe}$ suggest that these derivatives exhibit strong coupling between the two redox-active phenolates, where $[\text{Ni(Sal)}^\text{tBu}]^{**}$ is the most delocalized. On the basis of the electrochemical data, and additional experimental and theoretical studies, $[\text{Ni(Sal)}^\text{tBu}]^{**}$ has been assigned as a fully-delocalized Class III system. The $\Delta E_{1/2}$ of $[\text{Ni(Sal)}^\text{OMe}]^{**}$ is considerably lower than those of $[\text{Ni(Sal)}^\text{tBu}]^{**}$, suggesting a significant decrease in coupling between the redox-active units, which is reflected in its $K_c$. The $\Delta E_{1/2}$ and $K_c$ values for $[\text{Ni(Sal)}^\text{NMe2}]^{**}$ are even lower than those of $[\text{Ni(Sal)}^\text{tBu}]^{**}$ and $[\text{Ni(Sal)}^\text{OMe}]^{**}$, indicating that there is even less coupling between the two redox-active phenolates in this ligand system. While caution should be applied when relating $\Delta E_{1/2}$ and $K_c$ values to the degree of coupling in mixed-valence systems, these electrochemical results points to a difference in the
extent of delocalization of the ligand radical in \([\text{Ni(Sal)}^R]^+\), which was confirmed independently by further spectroscopic and theoretical methods.

### 2.3.3 Theoretical Characterization

#### 2.3.3.1 Theoretical Characterization

Density functional theory (DFT) calculations of \(\text{Ni(Sal)}^\text{tBu}\) and \(\text{Ni(Sal)}^\text{OMe}\) using the B3LYP functional are in good agreement with the solid state data (Table 2.2), predicting symmetric structures within ±0.03 Å of the experimental values. Such a symmetric structure was also predicted for \(\text{Ni(Sal)}^\text{NMe}_2\). The B3LYP functional has been used to probe the geometric and electronic structures of \([\text{Ni(Sal)}^\text{tBu}]^+\) and \([\text{Ni(Sal)}^\text{OMe}]^+\). For \([\text{Ni(Sal)}^\text{tBu}]^+\) a symmetric coordination sphere contraction is predicted, matching the experimental data. The B3LYP functional predicts a symmetric complex, in contrast to the experimental data (Table 2.2). The result for \([\text{Ni(Sal)}^\text{OMe}]^+\) is not unexpected due to the tendency of DFT calculations to favour more symmetric delocalized solutions. This delocalization effect has been previously observed in DFT calculations of symmetric oxidized Pd salen systems as well as oxidized Mn-salen systems. The addition of a counterion (SbF\(_6^-\) based on X-ray coordinates) to the calculation of \([\text{Ni(Sal)}^\text{OMe}]^+\) results in an asymmetric structure matching the experimental data. As we were interested in determining a computational method better suited to predicting the geometric and electronic structure of oxidized metal salen systems, the Coulomb-Attenuated Method (CAM-B3LYP) was investigated. The utility of this functional has been demonstrated in predicting the energies of delocalized systems as well as long-range charge transfer transitions. In the CAM approach the exchange interaction at short range is modelled with 0.19 Hartree-Fock (HF) and 0.81 Becke 1988 (B88), long-range interactions are modelled with 0.65 HF and 0.35 B88, and the intermediate region is described by a standard error function. The inclusion of HF character for CAM-B3LYP limits the prediction of an overly delocalized solution, a common issue in DFT calculations. DFT calculations using the CAM-B3LYP functional for neutral \(\text{Ni(Sal)}^\text{tBu}\) and \(\text{Ni(Sal)}^\text{OMe}\) are in good agreement with the solid state data (Table 2.1), predicting symmetric structures within ±
of the experimental values. A symmetric structure is also predicted for \( \text{Ni(Sal)}^{\text{NMe2}} \).

Table 2.2. Experimental and calculated coordination sphere metrical parameters for neutral \( \text{Ni(Sal)}^R \) in Å.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Ni-O1</th>
<th>Ni-O2</th>
<th>Ni-N1</th>
<th>Ni-N2</th>
<th>C-O1</th>
<th>C-O2</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ni(Sal)}^{\text{tBu}} ), X-ray ( ^{14} )</td>
<td>1.852</td>
<td>1.854</td>
<td>1.852</td>
<td>1.860</td>
<td>1.304</td>
<td>1.311</td>
</tr>
<tr>
<td>( \text{Ni(Sal)}^{\text{tBu}} ), B3LYP</td>
<td>1.846</td>
<td>1.846</td>
<td>1.848</td>
<td>1.848</td>
<td>1.304</td>
<td>1.304</td>
</tr>
<tr>
<td>( \text{Ni(Sal)}^{\text{tBu}} ), CAM-B3LYP</td>
<td>1.830</td>
<td>1.830</td>
<td>1.843</td>
<td>1.843</td>
<td>1.298</td>
<td>1.298</td>
</tr>
<tr>
<td>( \text{Ni(Sal)}^{\text{OMe}} ), X-ray ( ^{25} )</td>
<td>1.817</td>
<td>1.817</td>
<td>1.827</td>
<td>1.827</td>
<td>1.323</td>
<td>1.323</td>
</tr>
<tr>
<td>( \text{Ni(Sal)}^{\text{OMe}} ), B3LYP</td>
<td>1.847</td>
<td>1.847</td>
<td>1.847</td>
<td>1.847</td>
<td>1.305</td>
<td>1.305</td>
</tr>
<tr>
<td>( \text{Ni(Sal)}^{\text{OMe}} ), CAM-B3LYP</td>
<td>1.830</td>
<td>1.830</td>
<td>1.843</td>
<td>1.842</td>
<td>1.299</td>
<td>1.299</td>
</tr>
<tr>
<td>( \text{Ni(Sal)}^{\text{NMe2}} ), X-ray</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( \text{Ni(Sal)}^{\text{NMe2}} ), B3LYP</td>
<td>(1.846)</td>
<td>(1.846)</td>
<td>(1.847)</td>
<td>(1.847)</td>
<td>(1.305)</td>
<td>(1.305)</td>
</tr>
<tr>
<td>( \text{Ni(Sal)}^{\text{NMe2}} ), CAM-B3LYP</td>
<td>(1.829)</td>
<td>(1.829)</td>
<td>(1.842)</td>
<td>(1.843)</td>
<td>(1.299)</td>
<td>(1.299)</td>
</tr>
</tbody>
</table>

For the oxidized forms, a symmetric coordination sphere contraction is found for \( \text{[Ni(Sal)]}^{\text{Bu}+} \) using CAM-B3LYP, matching the result for the B3LYP functional (Table 2.3). The key advance is the CAM-B3LYP prediction of an asymmetric structure for \( \text{[Ni(Sal)]}^{\text{OMe}+} \) even in the absence of counterion, matching the experimental result (Table 2.3). The asymmetry in the coordination sphere bond lengths (Ni-O and Ni-N), as well as the asymmetry in the phenolate C-O bond lengths affords a theoretical prediction of phenoxy radical localization in \( \text{[Ni(Sal)]}^{\text{OMe}+} \). A similar result is observed for \( \text{[Ni(Sal)]}^{\text{NMe2}+} \) as the CAM-B3LYP functional predicts an asymmetric complex and phenoxy radical localization for this derivative (Table 2.3). Based on the recent work of Allard and co-workers\(^{64} \), the optimization of \( \text{[Ni(Sal)]}^{\text{NMe2}+} \) using the B3LYP functional with a polarized continuum model (PCM) for CH\(_2\)Cl\(_2\) (dielectric constant \( \varepsilon = 8.94 \)) was also explored.\(^{65-68} \) While this optimization method does lead to an asymmetric ligand radical structure, the time-dependent DFT (TD-DFT) predictions do not match the experimental electronic transitions.
Table 2.3. Experimental and calculated coordination sphere metrical parameters for oxidized \([\text{Ni(Sal)}^\text{R}]^{**}\) in Å.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Ni-O1</th>
<th>Ni-O2</th>
<th>Ni-N1</th>
<th>Ni-N2</th>
<th>C-O1</th>
<th>C-O2</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Ni(Sal)}^\text{tBu}]^{**}), X-ray (^{12})</td>
<td>1.827</td>
<td>1.831</td>
<td>1.824</td>
<td>1.843</td>
<td>1.298</td>
<td>1.302</td>
</tr>
<tr>
<td>([\text{Ni(Sal)}^\text{tBu}]^{**}), B3LYP</td>
<td>1.823</td>
<td>1.823</td>
<td>1.839</td>
<td>1.839</td>
<td>1.302</td>
<td>1.302</td>
</tr>
<tr>
<td>([\text{Ni(Sal)}^\text{OMe}]^{**}), CAM-B3LYP</td>
<td>1.801</td>
<td>1.800</td>
<td>1.828</td>
<td>1.828</td>
<td>1.299</td>
<td>1.299</td>
</tr>
<tr>
<td>([\text{Ni(Sal)}^\text{OMe}]^{**}), X-ray (^{25})</td>
<td>1.816</td>
<td>1.863</td>
<td>1.839</td>
<td>1.843</td>
<td>1.274</td>
<td>1.333</td>
</tr>
<tr>
<td>([\text{Ni(Sal)}^\text{OMe}]^{**}), B3LYP</td>
<td>1.830</td>
<td>1.830</td>
<td>1.841</td>
<td>1.841</td>
<td>1.301</td>
<td>1.301</td>
</tr>
<tr>
<td>([\text{Ni(Sal)}^\text{OMe}]^{**}), CAM-B3LYP</td>
<td>1.793</td>
<td>1.854</td>
<td>1.825</td>
<td>1.852</td>
<td>1.271</td>
<td>1.314</td>
</tr>
<tr>
<td>([\text{Ni(Sal)}^\text{NMe2}]^{**}), X-ray</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>([\text{Ni(Sal)}^\text{NMe2}]^{**}), B3LYP</td>
<td>1.834</td>
<td>1.834</td>
<td>1.841</td>
<td>1.841</td>
<td>1.299</td>
<td>1.299</td>
</tr>
<tr>
<td>([\text{Ni(Sal)}^\text{NMe2}]^{**}), CAM-B3LYP</td>
<td>1.859</td>
<td>1.798</td>
<td>1.852</td>
<td>1.825</td>
<td>1.269</td>
<td>1.310</td>
</tr>
</tbody>
</table>

2.3.3.2 Electronic Structures

B3LYP and CAM-B3LYP predicted spin density plots for \([\text{Ni(Sal)}^\text{R}]^{**}\) are shown in Figure 2.5, and their corresponding analysis are presented in Table 2.4. The spin density is delocalized across the ligand framework for \([\text{Ni(Sal)}^\text{tBu}]^{**}\), with a significant proportion on the Ni centre (> 15%), using both B3LYP and CAM-B3LYP. However, for \([\text{Ni(Sal)}^\text{OMe}]^{**}\) localization on Ring B is observed using CAM-B3LYP, with a significant decrease in spin density at the metal centre in comparison to \([\text{Ni(Sal)}^\text{tBu}]^{**}\). A further increase in ligand radical localization was observed for \([\text{Ni(Sal)}^\text{NMe2}]^{**}\) in comparison to \([\text{Ni(Sal)}^\text{OMe}]^{**}\), with a concomitant decrease in metal spin density. For \([\text{Ni(Sal)}^\text{OMe}]^{**}\) and \([\text{Ni(Sal)}^\text{NMe2}]^{**}\), the typical quinoidal bonding pattern for a phenoxy radical on one of the aromatic rings is observed (Ring B), with significant positive spin population at the Ophenoxy (\([\text{Ni(Sal)}^\text{OMe}]^{**}\): 25.6%, \([\text{Ni(Sal)}^\text{NMe2}]^{**}\): 20.3%), C\text{ortho}\ (\([\text{Ni(Sal)}^\text{OMe}]^{**}\): 23.3%, \([\text{Ni(Sal)}^\text{NMe2}]^{**}\): 9.8%), and C\text{para}\ (\([\text{Ni(Sal)}^\text{OMe}]^{**}\): 27.4%, \([\text{Ni(Sal)}^\text{NMe2}]^{**}\): 15.4%) positions.
Figure 2.5. Calculated spin density using the B3LYP functional for: (a) [Ni(Sal)\textsuperscript{tBu}]\textsuperscript{••}; (b) [Ni(Sal)\textsuperscript{OMe}]\textsuperscript{••} and (c) [Ni(Sal)\textsuperscript{NMe\textsubscript{2}}}\textsuperscript{••}. Calculated spin density using the CAM-B3LYP functional for: (d) [Ni(Sal)\textsuperscript{tBu}]\textsuperscript{••}; (e) [Ni(Sal)\textsuperscript{OMe}]\textsuperscript{••} and (f) [Ni(Sal)\textsuperscript{NMe\textsubscript{2}}}\textsuperscript{••}.

Table 2.4. B3LYP and CAM-B3LYP predicted spin density values for [Ni(Sal)\textsuperscript{R}]\textsuperscript{••}.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Spin Density on Ni</th>
<th>Spin Density on Ring A</th>
<th>Spin Density on Ring B</th>
<th>Spin Density on Ni</th>
<th>Spin Density on Ring A</th>
<th>Spin Density on Ring B</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ni(Sal)\textsuperscript{tBu}]\textsuperscript{••}</td>
<td>15.8%</td>
<td>42.3%</td>
<td>41.8%</td>
<td>15.7%</td>
<td>42.1%</td>
<td>42.1%</td>
</tr>
<tr>
<td>[Ni(Sal)\textsuperscript{OMe}]\textsuperscript{••}</td>
<td>8.9%</td>
<td>45.3%</td>
<td>45.4%</td>
<td>3.6%</td>
<td>5.2%</td>
<td>91.0%</td>
</tr>
<tr>
<td>[Ni(Sal)\textsuperscript{NMe\textsubscript{2}}}\textsuperscript{••}</td>
<td>5.0%</td>
<td>47.3%</td>
<td>47.4%</td>
<td>1.7%</td>
<td>2.3%</td>
<td>95.7%</td>
</tr>
</tbody>
</table>
Interestingly, a planar para-dimethylaminophenoxyl structure was predicted for [Ni(Sal)NMe$_2$]$^{2+}$, highlighting the participation of the nitrogen lone pair into the SOMO of the ligand radical (Figure 2.6). The spin population on the planar NMe$_2$ moiety (Ring B) is 30%, with negligible spin density on the NMe$_2$ unit of Ring A. Similarly, the spin density on the OMe moiety of Ring B is 11% versus ca. 0% for the OMe unit of Ring A. This data highlights participation of electron donating para-ring substituents in the asymmetric electronic structures predicted for [Ni(Sal)OMe]$^{2+}$ and [Ni(Sal)NMe$_2$]$^{2+}$. A similar effect has been recently studied in a series of oxidized para–thiolate substituted Cu-salen systems. Overall, phenoxyl radical localization, and the decrease in metal spin density observed for [Ni(Sal)R]$^{2+}$ match the trend in electron donating ability of the para-ring substituents.

Figure 2.6. DFT-optimized structure of [Ni(Sal)NMe$_2$]$^{2+}$. Note: Ring B contains a planar para-dimethylaminophenoxyl moiety, indicating the radical species localizes on that aromatic system.

2.3.4 Continuous Wave Electron Paramagnetic Resonance

The X-band EPR spectra of [Ni(Sal)R]$^{2+}$ collected at 20 K exhibit broad and essentially isotropic signals for all three radical complexes (Figure 2.7). The $g$-values are reported in Table 2.5, where all [Ni(Sal)R]$^{2+}$ complexes displayed signals between $g_{iso}$ 2.045 and 2.005. These $g$-values are intermediate between a Zn analogue [Zn(Sal)tBu]$^{2+}$ ($g_{iso} = 2.005$), which is representative for a coordinated phenoxy radical, and that observed for a Ni$^{iii}$ complex ($g_{av} = 2.13–2.17$). Importantly, the shift in $g$-value from the free electron value ($g_e = 2.002$) is consistent with the contribution of the metal d-orbitals to the SOMO of [Ni(Sal)tBu]$^{2+}$ and [Ni(Sal)OMe]$^{2+}$. The $g$-value for [Ni(Sal)NMe$_2$]$^{2+}$ ($g_{iso} = 2.005$) is similar to the Zn analogue [Zn(Sal)tBu]$^{2+}$ described above,
indicating very little metal contribution to SOMO of $[\text{Ni(Sal)}^{\text{NMe}_2}]^{\ddagger\ddagger}$, which is consistent with the predicted metal spin density values (Table 2.5).

![Figure 2.7. X-band EPR spectra for: $[\text{Ni(Sal)}^{\text{tBu}}]^{\ddagger\ddagger}$ (black), $[\text{Ni(Sal)}^{\text{OMe}}]^{\ddagger\ddagger}$ (red) and $[\text{Ni(Sal)}^{\text{NMe}_2}]^{\ddagger\ddagger}$ (blue) in CH$_2$Cl$_2$ at 20 K. Conditions: Frequency: 9.385 GHz for $[\text{Ni(Sal)}^{\text{tBu}}]^{\ddagger\ddagger}$, 9.382 GHz for $[\text{Ni(Sal)}^{\text{OMe}}]^{\ddagger\ddagger}$ and 9.382 GHz for $[\text{Ni(Sal)}^{\text{NMe}_2}]^{\ddagger\ddagger}$; Power: 0.2 mW; modulation frequency: 100 kHz; amplitude 0.2 mT.]

Additional experimental support for ligand radical localization in $[\text{Ni(Sal)}^{\text{NMe}_2}]^{\ddagger\ddagger}$ is obtained by analysis of the hyperfine pattern at 298 K (Figure 2.8). The EPR spectrum of $[\text{Ni(Sal)}^{\text{tBu}}]^{\ddagger\ddagger}$ and $[\text{Ni(Sal)}^{\text{OMe}}]^{\ddagger\ddagger}$ display broad isotropic ligand radical signals, similar to that observed at 20 K, while the spectrum of $[\text{Ni(Sal)}^{\text{NMe}_2}]^{\ddagger\ddagger}$ at 298 K provides additional hyperfine interactions as detailed in Table 2.5. It is noteworthy that the hyperfine splitting is in accord with the pattern previously reported for an asymmetric Ni$^{\text{III}}$ radical salen complex involving a single para-dimethylaminophenoxyl moiety. The spectrum for $[\text{Ni(Sal)}^{\text{NMe}_2}]^{\ddagger\ddagger}$ was best-fit by considering two N atoms ($A_N = 19.2$ MHz, $A_{N_2} = 8.3$ MHz), six identical H atoms ($A_{H_1} = 19.4$ MHz) and two additional H atoms ($A_{H_2} = 3.9$ MHz, $A_{H_3} = 2.4$ MHz). The assignment of the hyperfine coupling constants is as follows: $A_N$ and $A_{H_1}$ are ascribed to the NMe$_2$ substituent on the ligand radical ring system, with
the AH₂ and AH₃ corresponding to the meta-hydrogens on the aromatic system. Finally, the remaining AN₂ likely arises from an imine nitrogen (Figure 2.8 and Table 2.5). It is important to note that the EPR spectrum of [Ni(Sal)NMe₂]⁺ could not be fit satisfactorily as a symmetrically-delocalized ligand radical by considering twice the number of nuclei. Thus this EPR data for provides experimental evidence for ligand radical localization for [Ni(Sal)NMe₂]⁺.

Figure 2.8. X-band EPR spectra for: (a) [Ni(Sal)IBu]⁺; (b) [Ni(Sal)OMe]⁺ and (c) [Ni(Sal)NMe₂]⁺ in CH₂Cl₂ at 298 K. Experimental data: black, Simulation: red. Conditions: Frequency: 9.379 GHz for [Ni(Sal)IBu]⁺, 9.383 GHz for [Ni(Sal)OMe]⁺ and 9.381 GHz for [Ni(Sal)NMe₂]⁺; Power: 2.0 mW; modulation frequency: 100 kHz; amplitude 0.6 mT for [Ni(Sal)IBu]⁺ and [Ni(Sal)OMe]⁺, 0.2 mT for [Ni(Sal)NMe₂]⁺.
Table 2.5. Correlation of X-band EPR isotropic g-values with predicted spin density on Ni for \([\text{Ni(Sal)}^R]^+\).

<table>
<thead>
<tr>
<th>Complex</th>
<th>Predicted Spin density on Ni (CAM-B3LYP)</th>
<th>(g)-value ((298 \text{ K}))</th>
<th>(g)-value ((20 \text{ K}))</th>
<th>Simulated A-values ((\text{MHz}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Ni(Sal)}^t\text{Bu}]^+)</td>
<td>15.7%</td>
<td>2.045</td>
<td>2.044</td>
<td>-</td>
</tr>
<tr>
<td>([\text{Ni(Sal)}^\text{OMe}]^+)</td>
<td>3.6%</td>
<td>2.023</td>
<td>2.023</td>
<td>-</td>
</tr>
<tr>
<td>([\text{Ni(Sal)}^\text{NMe}_2]^+)</td>
<td>1.7%</td>
<td>2.005</td>
<td>2.004</td>
<td>AN(_1) = 19.2; AN(_2) = 8.3; 6 AH(_1) = 19.4; AH(_2) = 3.9; AH(_3) = 2.4</td>
</tr>
</tbody>
</table>

2.3.5 Pulsed Electron Paramagnetic Resonance

To gain further insight into the structural surroundings of the unpaired electron, 2D hyperfine-sublevel correlation experiments (2D-HYSCORE) on \([\text{Ni(Sal)}]^+\) were conducted. This two-dimensional pulsed EPR technique allows for the measurement of quadrupolar and hyperfine couplings of the electronic spin with surrounding nuclei, which are identified by their unique Larmor nuclear frequencies to allow for the proper assignment of couplings with a variety of nuclei (i.e. \(^1\text{H}\), \(^14\text{N}\), or \(^19\text{F}\)).\(^73\) The 2D-HYSCORE experiment shows the spectrum found in the 1D experiment along two axes, where cross-peaks appear for two coupled nuclei. Peaks are separated into two quadrants, namely the (+,-) and (+,+) quadrants, depending on the strength of the hyperfine interaction. The (+,-) quadrant displays strong hyperfine couplings where \(|A_{\text{iso}}| >> 2\nu_I\) (where \(A_{\text{iso}}\) is the isotropic hyperfine coupling and \(\nu_I\) is the Larmor nuclear frequency), and the (+,+) quadrant displays strong hyperfine couplings with \(|A_{\text{iso}}| << 2\nu_I\).

The 2D-HYSCORE spectrum of \([\text{Ni(Sal)}^{t\text{Bu}}]^+\) recorded at 4 K is shown in Figure 2.9. In the (+,-) quadrant, nitrogen features \((l_N = 1, \nu_I = 1.1 \text{ MHz})\) were observed, with two pairs of cross peaks (denoted sq\(^{14}\text{N}\) and dq\(^{14}\text{N}\)) assigned to single quantum (sq, selection rule \(\Delta M_I = 1\)) and double quantum (dq, selection rule \(\Delta M_I = 2\)) correlations, as expected for a \(l_N = 1\) nuclei. Thus, the coupling in this quadrant arises from a single population of equivalent \(^{14}\text{N}\) nuclei of the two salicylidene nitrogens. In the (+,+) quadrant, two distinct pairs of cross-peaks centered at \(\nu_I = 15 \text{ MHz}\) (Larmor nuclear frequency of \(^1\text{H}\)) with \(A_{\text{iso}}\) of 8.8 and 7.2 MHz were observed (Inset, Figure 2.9), which
are assigned to the protons located on the salicylidene moieties. In addition, a pair of
cross peaks centered at $\nu_1 = 14$ MHz (Larmor nuclear frequency of $^{19}$F) with weak
hyperfine coupling of $0.8$ MHz were also observed, suggesting a weak interaction
between $\text{[Ni(Sal)}^{\text{Bu}}}^\text{•}$ and the $\text{SbF}_6^-$ counterion (Inset, Figure 2.9). Taken together, this
demonstrates that the unpaired electron is distributed uniformly over the entire ligand
framework, supporting its assignment as a Class III delocalized compound.

Figure 2.9. 2D-HYSCORE spectra of $\text{[Ni(Sal)}^{\text{Bu}}]^\text{•}$ at the $g = 2.045$ value of the
continuous-wave spectrum in CH$_2$Cl$_2$ at 4 K. Insert: Magnification of the
(+,+)$) quadrant.

The 2D-HYSCORE spectrum of $\text{[Ni(Sal)}^{\text{OMe}}]^\text{•}$ recorded at 4 K is shown in Figure
2.10. In comparison to the spectrum of $\text{[Ni(Sal)}^{\text{Bu}}]^\text{•}$, an additional pair of cross-peaks in
the (+,-) quadrant was observed, corresponding to a new dq$^{14}$N transition. This
suggests coupling between the unpaired electron and two unique sets $^{14}$N nuclei, an
indication of non-equivalence between the two salicylidene moieties due to an
asymmetric electronic structure. In the (+,+)$)$ quadrant, a single pair of cross peaks
centered at $\nu_1 = 15$ MHz with hyperfine coupling of $7.8$ MHz was detected and attributed
to protons on the salicylidene moiety, while no signal for the $^{19}$F nucleus was observed.
Taken together, the HYSCORE data of $\text{[Ni(Sal)}^{\text{OMe}}]^\text{•}$ suggests that the unpaired electron
is not uniformly distributed as observed for $\text{[Ni(Sal)}^{\text{Bu}}]^\text{•}$, providing further evidence that
that the radical is at least partially localized on one salicylidene ring.
Figure 2.10. 2D-HYSCORE spectra of $[\text{Ni(Sal)}^{\text{OMe}}]^{\text{••}}$ at the $g = 2.023$ value of the continuous-wave spectrum in CH$_2$Cl$_2$ at 4 K. Insert: Magnification of the (+,+)$\omega_1$ quadrant.

The 2D-HYSCORE spectrum of $[\text{Ni(Sal)}^{\text{NMe}_2}]^{\text{••}}$ recorded at 4 K differs dramatically in comparison to the data for $[\text{Ni(Sal)}^{\text{tBu}}]^{\text{••}}$ and $[\text{Ni(Sal)}^{\text{OMe}}]^{\text{••}}$ (Figure 2.11). A unique peak centered at the $^{14}\text{N}$ Larmor nuclear frequency was observed, and is characterized as a dipolar interaction between the unpaired electron and distant $^{14}\text{N}$ nuclei. Surprisingly, very little information about the hyperfine or dipolar couplings were obtained from the HYSCORE pattern of $[\text{Ni(Sal)}^{\text{NMe}_2}]^{\text{••}}$, likely due to experimental limitations. The absence of large anisotropic couplings in the HYSCORE spectra have been previously observed, and have been ascribed to low modulation depth and/or experimental bandwidth limitations. This suggests that $[\text{Ni(Sal)}^{\text{NMe}_2}]^{\text{••}}$ is a fully localized radical with the major part of the spin density distributed on one para-NMe$_2$ group, where strong hyperfine coupling for the nuclei discussed is expected, but could not be measured experimentally. This data, when taken together with other data discussed in this Chapter, are thus consistent with localization of the ligand radical in $[\text{Ni(Sal)}^{\text{NMe}_2}]^{\text{••}}$. 
2.3.6 Resonance Raman Spectroscopy

Resonance Raman (rR) spectra of Ni(Sal)$^{OMe}$ and Ni(Sal)$^{NMe2}$, and their one-electron oxidized forms, [Ni(Sal)$^{OMe}$]$^{+•}$ and [Ni(Sal)$^{NMe2}$]$^{+•}$, were carried out at excitation wavelengths of both 413.1 nm (24200 cm$^{-1}$) and 457.9 nm (21800 cm$^{-1}$), respectively, due to their different $\lambda_{max}$. No significant difference in the 1400 to 1700 cm$^{-1}$ range was evident in the rR spectrum using the different excitation energies. Ni(Sal)$^{tBu}$ and [Ni(Sal)$^{tBu}$]$^{+•}$ have been previously studied by rR, where the phenolate Raman bands were replaced by two intense phenoxyl radical $\nu_{7a}$ (C-O stretching vibration of a phenoxyl radical) and $\nu_{8a}$ (C$_{ortho}$-C$_{meta}$ stretching vibration of a phenoxyl radical) bands upon oxidation. The rR spectra for both [Ni(Sal)$^{OMe}$]$^{+•}$ and [Ni(Sal)$^{NMe2}$]$^{+•}$ exhibit significant changes in comparison to their neutral counterparts: in both complexes a new intense band appears at 1612 cm$^{-1}$, which is assigned to the phenoxyl radical $\nu_{8a}$ vibration of [Ni(Sal)$^{OMe}$]$^{+•}$ and [Ni(Sal)$^{NMe2}$]$^{+•}$ (Figure 2.12). Interestingly, phenolate bands were also present in the spectra of both [Ni(Sal)$^{OMe}$]$^{+•}$ and [Ni(Sal)$^{NMe2}$]$^{+•}$, providing evidence for the formation of a localized ligand radical. Indeed, a similar pattern was also observed in the spectrum of a one-electron oxidized Pd$^{II}$-salen complex, which was described as a Class II/III borderline system. It should be noted that the $\nu_{7a}$ band of the phenoxyl radical in [Ni(Sal)$^{OMe}$]$^{+•}$, which is expected to be found
at ca. 1500 cm\(^{-1}\), could not be detected. For \([\text{Ni(Sal)}^{\text{NMe2}}}\)\(^{++}\), the band at 1517 cm\(^{-1}\) was tentatively assigned as the \(\nu_{\tau a}\) band, which is in good agreement with the value of the free para-aminophenoxyl radical.\(^{77}\) The absence of the \(\nu_{\tau a}\) band for certain metal coordinated phenoxyl radical complexes has been previously reported, and could be due to the correlation of vibronic coupling with the \(\pi - \pi^*\) transition of the phenoxyl radical.\(^{78}\) The rR results support the assignment of \([\text{Ni(Sal)}^{\text{OMe}}}\)\(^{++}\) and \([\text{Ni(Sal)}^{\text{NMe2}}}\)\(^{++}\) as localized Ni\(^{II}\)(phenolate)(phenoxyl) complexes, in line with other experimental and theoretical data.

\[\text{Figure 2.12.} \quad \text{Resonance Raman spectra for: (a) Ni(Sal)}^{\text{OMe}}\) (black) and \([\text{Ni(Sal)}^{\text{OMe}}}\)\(^{++}\) (red) and (b) Ni(Sal)\(^{NMe2}\) (black) and \([\text{Ni(Sal)}^{\text{NMe2}}}\)\(^{++}\) (red).

Note: Spectra for Ni(Sal)\(^{OMe}\) and \([\text{Ni(Sal)}^{\text{OMe}}}\)\(^{++}\) collected at \(\lambda_{\text{ex}} = 413.1\) nm, Ni(Sal)\(^{NMe2}\) and \([\text{Ni(Sal)}^{\text{NMe2}}}\)\(^{++}\) collected at \(\lambda_{\text{ex}} = 457.9\) nm. \(T = 213\) K.

2.3.7 Electronic Spectroscopy

The electronic absorption spectra of Ni(Sal)\(^{tBu}\), Ni(Sal)\(^{OMe}\) and Ni(Sal)\(^{NMe2}\) are typical of low-spin d\(^{8}\) square-planar Ni\(^{II}\) bis-phenolate salen complexes (Figure 2.13-2.15), and no absorption was observed at energies lower than 17000 cm\(^{-1}\). Upon oxidation NIR transitions are observed, and the spectra for \([\text{Ni(Sal)}^{tBu}]^{++}\) and \([\text{Ni(Sal)}^{OMe}]^{++}\) are similar to those reported by Stack and co-workers\(^{12}\), and Fujii and co-workers\(^{39}\), respectively (Figures 2.13 and 2.14). The NIR bands for \([\text{Ni(Sal)}^{tBu}]^{++}\) (\(\lambda_{\text{max}} =\)
4700 cm–1) and [Ni(Sal)OME]⁺⁺ (λ_max = 4600 cm–1) occur at similar energies, but the band for [Ni(Sal)NMe2]⁺⁺ (λ_max = 11000 cm–1) is observed at a higher energy and is much broader (Figure 2.15).

**Figure 2.13.** UV-Vis-NIR spectrum of Ni(Sal)tBu (black) and [Ni(Sal)tBu]⁺⁺ (red) in CH₂Cl₂ at 298 K. Note: Vertical green bar indicates the energy of the most intense TD-DFT calculated transition at low energy.
Figure 2.14. UV-Vis-NIR spectrum of Ni(Sal)$_{OMe}$ (black) and [Ni(Sal)$_{OMe}$]$^{+•}$ (red) in CH$_2$Cl$_2$ at 298 K. 
Note: Vertical green bar indicates the energy of the most intense TD-DFT calculated transition at low energy.

Figure 2.15. UV-Vis-NIR spectrum of Ni(Sal)$_{NMe2}$ (black) and [Ni(Sal)$_{NMe2}$]$^{+•}$ (red) in CH$_2$Cl$_2$ at 298 K. 
Note: Vertical green bar indicates the energy of the most intense TD-DFT calculated transition at low energy.
Analysis of the energy, intensity, and shape of NIR bands can reveal information regarding the degree of localization in mixed-valence systems.\(^{30}\) The NIR bands herein were evaluated using the Hush equation (Eq. 4), where a Class III delocalized system by the Robin-Day classification generally displays a sharp ($\Delta \nu_{1/2} \leq 2000 \text{ cm}^{-1}$) IVCT transition.\(^{30}\)

$$\Delta \nu_{1/2} = \sqrt{16 \ln 2 RT \nu_{\text{max}}}$$  \hspace{1cm} (4)

Indeed, a sharp ($\Delta \nu_{1/2} = 660 \text{ cm}^{-1}$ (experimental): $\Delta \nu_{1/2} = 3280 \text{ cm}^{-1}$ (calculated)) and intense ($\varepsilon = 21600 \text{ cm}^{-1}$) NIR transition for $[\text{Ni(Sal)}^{tBu}]^{\text{II}^+}$ indicates that the ligand radical is fully delocalized over the entire ligand scaffold, as previously reported (Table 2.6).\(^{12}\) The broader ($\Delta \nu_{1/2} = 1250 \text{ cm}^{-1}$ (experimental): $\Delta \nu_{1/2} = 3260 \text{ cm}^{-1}$ (calculated)) and moderately intense ($\varepsilon = 12700 \text{ cm}^{-1}$) NIR transition observed for $[\text{Ni(Sal)}^{\text{OMe}}]^{\text{II}^+}$ suggests that the radical is more localized on one of the two redox-active phenolates, consistent with the predicted spin density and solid state data.\(^{28}\) Fujii and co-workers have assigned $[\text{Ni(Sal)}^{\text{OMe}}]^{\text{II}^+}$ as a borderline Class II/III system based on band shape analysis.\(^{39}\) Interestingly, their reported $\Delta \nu_{1/2}$ (2900 cm\(^{-1}\)) is larger than that reported in this work, with the NIR band shape also differing. This difference is attributed to the presence of a large excess of tetrabutylammonium triflate supporting electrolyte present in their experimental protocol necessary for electrochemical oxidation. The very broad ($\Delta \nu_{1/2} = 8630 \text{ cm}^{-1}$ (experimental): $\Delta \nu_{1/2} = 5090 \text{ cm}^{-1}$ (calculated)) NIR transition of $[\text{Ni(Sal)}^{\text{NMe2}}]^{\text{II}^+}$ suggests significant localization of the ligand radical on one of the electron rich phenolate moieties, leading to the assignment of $[\text{Ni(Sal)}^{\text{NMe2}}]^{\text{II}^+}$ as a Class II mixed valence complex.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\nu_{\text{max}}$ (cm(^{-1}))</th>
<th>$\varepsilon$ (M(^{-1}) cm(^{-1}))</th>
<th>$\Delta \nu_{1/2}$ (Experimental, cm(^{-1}))</th>
<th>$\Delta \nu_{1/2}$ (Calculated, cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Ni(Sal)}^{tBu}]^{\text{II}^+}$</td>
<td>4700</td>
<td>21600</td>
<td>660</td>
<td>3280</td>
</tr>
<tr>
<td>$[\text{Ni(Sal)}^{\text{OMe}}]^{\text{II}^+}$</td>
<td>4600</td>
<td>12700</td>
<td>1250</td>
<td>3260</td>
</tr>
<tr>
<td>$[\text{Ni(Sal)}^{\text{NMe2}}]^{\text{II}^+}$</td>
<td>11000</td>
<td>2550</td>
<td>8630</td>
<td>5090</td>
</tr>
</tbody>
</table>
Variable temperature UV-Vis-NIR data for $[\text{Ni(Sal)}^\text{NMe2}]^{\text{**}}$ demonstrated that temperature does not significantly affect the intensity or the shape of its NIR transition, indicating that ligand radical localization is not temperature-dependant (Figure 2.16). The energy and intensity of the NIR transitions for $[\text{Ni(Sal)}^\text{R}]^{\text{**}}$, in conjunction with their NIR band shape analysis, further demonstrate ligand radical localization for complexes with higher electron-donating ability at the para-ring position.

![Variable Temperature UV-Vis-NIR spectrum of $[\text{Ni(Sal)}^\text{NMe2}]^{\text{**}}$ in CH$_2$Cl$_2$.](image)

**Figure 2.16.** Variable Temperature UV-Vis-NIR spectrum of $[\text{Ni(Sal)}^\text{NMe2}]^{\text{**}}$ in CH$_2$Cl$_2$.

### 2.3.7 Theoretical Analysis of the NIR transitions

Time-Dependent Density Functional Theory (TD-DFT)$^{50-51}$ calculations using both B3LYP and CAM-B3LYP functionals were undertaken in order to gain insight into the absorption spectra of $[\text{Ni(Sal)}^\text{R}]^{\text{**}}$. The B3LYP functional predicts intense NIR bands for all three oxidized complexes (Table 2.7). The B3LYP-predicted energy and intensity for the series ($[\text{Ni(Sal)}^\text{NMe2}]^{\text{**}} > [\text{Ni(Sal)}^\text{OMe}]^{\text{**}} > [\text{Ni(Sal)}^\text{tBu}]^{\text{**}}$) does not match the experimental results and highlights the effect of over-delocalization on the predicted NIR transitions. Calculations employing the CAM-B3LYP functional better predicts both the geometric and electronic properties in this series. Importantly, calculations using the CAM-B3LYP functional correctly predict the absence of low energy electronic transitions.
for Ni(Sal)\textsuperscript{R}, and a series of low energy transitions for [Ni(Sal)\textsuperscript{R}]\textsuperscript{2+} (Figure 2.13-2.15 vertical green bars, Table 2.7).

**Table 2.7.** Comparison of the experimental and calculated TD-DFT NIR transitions for [Ni(Sal)\textsuperscript{R}]\textsuperscript{2+} using the B3LYP and CAM-B3LYP functional.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Transition ( MO )</th>
<th>Energy ( cm\textsuperscript{-1} )</th>
<th>Predicted Oscillator Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Exp.</td>
<td>Calc.</td>
</tr>
<tr>
<td>[Ni(Sal)\textsuperscript{tBu}]\textsuperscript{2+}, B3LYP</td>
<td>β–HOMO → β–LUMO</td>
<td>4700</td>
<td>5700</td>
</tr>
<tr>
<td>[Ni(Sal)\textsuperscript{tBu}]\textsuperscript{2+}, CAM-B3LYP</td>
<td>β–HOMO → β–LUMO</td>
<td>4700</td>
<td>3100</td>
</tr>
<tr>
<td>[Ni(Sal)\textsuperscript{OMe}]\textsuperscript{2+}, B3LYP</td>
<td>β–HOMO → β–LUMO</td>
<td>4600</td>
<td>5000</td>
</tr>
<tr>
<td>[Ni(Sal)\textsuperscript{OMe}]\textsuperscript{2+}, CAM-B3LYP</td>
<td>β–HOMO → β–LUMO</td>
<td>4600</td>
<td>7300</td>
</tr>
<tr>
<td>[Ni(Sal)\textsuperscript{NMe\textsubscript{2}}]\textsuperscript{2+}, B3LYP</td>
<td>β–HOMO → β–LUMO</td>
<td>11000</td>
<td>4200</td>
</tr>
<tr>
<td>[Ni(Sal)\textsuperscript{NMe\textsubscript{2}}]\textsuperscript{2+}, CAM-B3LYP</td>
<td>β–HOMO → β–LUMO</td>
<td>11000</td>
<td>9400</td>
</tr>
</tbody>
</table>

The calculated energy of the NIR bands shift to higher energy as phenoxy radical localization is increased in [Ni(Sal)\textsuperscript{R}]\textsuperscript{2+} (Table 2.7). Using the B3LYP functional to predict the electronic transitions using the CAM-B3LYP optimized geometries of [Ni(Sal)\textsuperscript{R}]\textsuperscript{2+} fails to afford the observed pattern of electronic transitions, further highlighting the sensitivity of the IVCT band towards electronic delocalization. Analysis of the orbitals involved in the intense low energy NIR bands for [Ni(Sal)\textsuperscript{R}]\textsuperscript{2+} reveals that each is predicted to be a β–HOMO → β–LUMO transition (Figure 2.17). Each band was specifically assigned as ligand to ligand charge transfer (LLCT) transitions, with the orbitals for [Ni(Sal)\textsuperscript{tBu}]\textsuperscript{2+} being delocalized across the ligand framework as reported previously (Figure 2.17).\textsuperscript{12} In contrast, the NIR bands for [Ni(Sal)\textsuperscript{OMe}]\textsuperscript{2+} and [Ni(Sal)\textsuperscript{NMe\textsubscript{2}}]\textsuperscript{2+} are predicted to be IVCT bands with transfer of electron density between the phenolate to phenoxy moieties (Figure 2.17). Based on the CAM-B3LYP calculation results, both [Ni(Sal)\textsuperscript{OMe}]\textsuperscript{2+} and [Ni(Sal)\textsuperscript{NMe\textsubscript{2}}]\textsuperscript{2+} are predicted to be in the Class II regime, while [Ni(Sal)\textsuperscript{tBu}]\textsuperscript{2+} is a Class III intervalence compound.
Ligand radical localization in a series of symmetric oxidized Ni$^{II}$-salen systems was correlated with the electron donating ability of the para-ring substituents ($[\text{Ni(Sal)}^{\text{tBu}}]^{2+} < [\text{Ni(Sal)}^{\text{OMe}}]^{2+} < [\text{Ni(Sal)}^{\text{NMe2}}]^{2+}$). As expected, the more electron rich the ligand the easier it is to oxidize the complex, and the less metal character observed in the SOMO in the oxidized form. Remarkably, both $[\text{Ni(Sal)}^{\text{OMe}}]^{2+}$ and $[\text{Ni(Sal)}^{\text{NMe2}}]^{2+}$ exhibited significant localization of the radical on one of two phenolate moieties. The locus of oxidation is evidenced independently by electrochemistry, UV-Vis-NIR, rR, EPR and 2D-HYSCORE spectroscopies. Computational studies by DFT calculations using the CAM-B3LYP functional were utilized to describe the electronic structures of $[\text{Ni(Sal)}]^{2+}$, where ligand radical localization and the associated trend in NIR electronic transitions was established. While the computational results using the CAM-B3LYP functional may actually provide an ‘over-localized’ description, especially in the case of $[\text{Ni(Sal)}^{\text{OMe}}]^{2+}$, the CAM–B3LYP functional offers considerable improvement in this case.
over the commonly used B3LYP functional, which favors overly delocalized and symmetric structures. The combined experimental and theoretical results highlight the influence of the metal ion bridge in mediating the coupling between the two redox-active phenolates, where the energy match between the Ni d\textsubscript{xz} orbital and the appropriate ligand MO ([Ni(Sal)\textsuperscript{tBu}]\textsuperscript{2+} > [Ni(Sal)\textsuperscript{OMe}]\textsuperscript{2+} > [Ni(Sal)\textsuperscript{NMe\textsubscript{2}}]\textsuperscript{2+}) dictates the overlap through the central metal ion. For the less electron-rich ligand in [Ni(Sal)\textsuperscript{tBu}]\textsuperscript{2+}, there is significant contribution of the metal to the SOMO due to ideal energy matching between the metal and ligand orbitals. Vibronic coupling then allows for significant communication between the two aromatic rings, and delocalization of the electron hole. Consequently, the radical species [Ni(Sal)\textsuperscript{tBu}]\textsuperscript{2+} is a Robin-Day Class III (fully delocalized) intervalence complex. For the more electron-rich ligands ([Ni(Sal)\textsuperscript{OMe}]\textsuperscript{2+} and [Ni(Sal)\textsuperscript{NMe\textsubscript{2}}]\textsuperscript{2+}) the energy match between the metal and ligand orbitals is less optimal as the ligand orbitals are higher in energy. This results in a decrease in metal ion character in the SOMO, especially for [Ni(Sal)\textsuperscript{NMe\textsubscript{2}}]\textsuperscript{2+}. The metal bridge thus does not efficiently promote communication between the rings, resulting in ligand radical localization. From the UV-Vis-NIR experiments [Ni(Sal)\textsuperscript{OMe}]\textsuperscript{2+} and [Ni(Sal)\textsuperscript{NMe\textsubscript{2}}]\textsuperscript{2+} are assigned as Robin-Day Class II/III borderline and Class II intervalence systems respectively. In addition, the NMe\textsubscript{2} substituent, and to a lesser extent the OMe substituent, participate in the localization of the electron hole, providing an alternate stabilization mechanism by donating its lone pair into the \(\pi\)-system of the phenoxyl radical. These new results provide a basis for the rational design of mixed-valence systems involving a metal bridge, and serve as instructive models for the understanding of radical active sites in metalloproteins. For future directions, see Chapter 6.

2.5 References


54. Gorelsky, S. I. AOMix, Program for Molecular Orbital Analysis.


3.1 Introduction

The synthesis and characterization of a series of Ni III-salen complexes and their one-electron oxidized counterparts was outlined in Chapter 2, where the para-substituent on the phenolate moiety varied from weakly to strongly electron-donating (tBu < OMe < NMe₂). While an electron-rich ligand is desirable for the formation of oxidized species at lower oxidation potential, electron-deficient ligands are also of interest as a means to increase the electrophilicity of the metal center for substrate binding and activation. 1-2 As these ligands bearing electron-withdrawing substituents have higher oxidation potentials, there have been fewer studies on complexes involving such ligands to form ligand radical cations, especially in the case of salen ligands. While an electron-deficient salen ligand is less effective as a source of redox equivalents, using electron-withdrawing groups to tune the electrophilicity of the metal center is of significant interest towards optimizing reactivity at the metal center, and thus warranted investigation.

3.2 Experimental

3.2.1 Materials

All chemicals used were of the highest grade available and were further purified whenever necessary. 3 2-tert-butyl-4-trifluoromethylphenol was prepared from commercially available 4-trifluoromethylphenol by reported procedures. 4 The aminium
radical chemical oxidant \([\text{N(C}_6\text{H}_3\text{Br}_2)_3]^+\text{[SbF}_6]^-\) was synthesized according to published protocols.\(^5\)-\(^7\)

### 3.2.2 Instrumentation

Electronic spectra were obtained on a Cary 5000 spectrophotometer with a custom-designed immersion fiber-optic probe with variable path length (1 and 10 mm; Hellma, Inc.). Constant temperatures were maintained by a dry ice/acetone bath. Solvent contraction was accounted for in all variable-temperature studies. Cyclic voltammetry (CV) was performed on a PAR-263A potentiometer, equipped with an Ag wire reference electrode, a platinum disk working electrode and a Pt counter electrode with \(^{\text{n}}\text{Bu}_4\text{NCIO}_4\) (0.1 M) solutions in \(\text{CH}_2\text{Cl}_2\). Decamethylferrocene was used as an internal standard.\(^8\) \(^1\)H NMR spectra were recorded on a Bruker AV-500 instrument. Mass spectra (ESI positive ion or ESI negative ion) were obtained on an Agilent 6210 TOF ESI-MS instrument. Elemental analyses (C, H, N) were performed by Mr. Paul Mulyk at Simon Fraser University on a Carlo Erba EA1110 CHN elemental analyzer. All EPR spectra were collected using a Bruker EMXplus spectrometer operating with a premiumX X-band (~9.5 GHz) microwave bridge. Low temperature measurements of frozen solutions used a Bruker helium temperature-control system and a continuous flow cryostat. Samples for X-band measurements were placed in 4 mm outer-diameter sample tubes with sample volumes of ~300 μL. Spectra at 195 K were collected in capillary tubes, which were placed inside a standard EPR tube.

### 3.2.3 X-ray Structure Determination

Single crystal X-ray crystallographic analysis of \(\text{Ni(Sal)}^{\text{CF}_3}\) and \(\text{Cu(Sal)}^{\text{CF}_3}\) was performed on a Bruker X8 APEX II diffractometer with graphite monochromated Mo-K\(\alpha\) radiation. An orange block (\(\text{Ni(Sal)}^{\text{CF}_3}\)) or a dark purple prism (\(\text{Cu(Sal)}^{\text{CF}_3}\)) crystal was mounted on a glass fibre. The data were collected at 150 ± 0.1 K to a maximum 2θ value of 55.0˚. Data were collected in a series of \(\phi\) and \(\omega\) in 0.50˚ widths with 10.0 second exposures. The crystal-to-detector distance was 50 mm. The structure was solved by direct methods (SIR92)\(^9\) and refined by least-squares procedures using CRYSTALS (v14.40b)\(^10\) or ShelXle.\(^11\) All non-hydrogen atoms were refined...
anisotropically. All C-H hydrogen atoms were placed in calculated positions but were not refined. All crystal structure plots were produced using ORTEP-3 and rendered with POV-Ray (v.3.6.2). A summary of the crystal data and experimental parameters for structure determinations are given in Appendix 1.

3.2.4 Oxidation Protocols

Under an inert atmosphere at 195 K, 500 µL of a CH₂Cl₂ solution of the metal complex (4.6 mM) was added to 3.0 mL of CH₂Cl₂. Monitored by UV-Vis-NIR, a saturated solution of [N(C₆H₃Br₂)₃]⁺[SbF₆]⁻ in CH₂Cl₂ was added in 60 µL additions resulting in clean conversion to the respective one-electron oxidized species.

3.2.5 Calculations

Geometry optimizations were performed using the Gaussian 09 program (Revision D.01),¹² the B3LYP¹³-¹⁴ functional with a polarized continuum model (PCM) for CH₂Cl₂ (dielectric ε = 8.94)¹⁵-¹⁸, and the 6-31G(d) basis set on all atoms. A symmetric structure was used as a starting point for all geometry optimizations. Frequency calculations at the same level of theory confirmed that the optimized structures were located at a minimum on the potential energy surface. Single point calculations were performed using the B3LYP functional and the TZVP basis set of Ahlrichs on all atoms.¹³-¹⁴ The intensities of the 30 lowest-energy electronic transitions were calculated by TD-DFT¹⁹-²⁰ at the B3LYP/TZVP level. The above calculations were also completed using the CAM-B3LYP²¹-²² functional for comparison. AOMix²³-²⁵ was used for determining atomic orbital compositions employing Mulliken Population Analysis.

3.2.6 Synthesis

3-tert-Butyl-5-trifluoromethylsalicylaldehyde:
To a solution of 2-tert-butyl-4-trifluoromethylphenol (1.50 g, 6.87 mmol) in trifluoroacetic acid (30 mL) was added hexamethylenetetramine (1.06 g, 7.56 mmol). The reaction mixture was stirred at reflux for 16 hours, and then it was cooled to room temperature and water (30 mL) was added. This solution was cooled and extracted with CH₂Cl₂ (3 x 50 mL), and the organic phase was dried over Na₂SO₄, and the filtrate was concentrated in vacuo. The crude product was subject to flash column chromatography using 4:1 CHCl₃ : hexanes as the eluent to afford a pale yellow oil. Yield: 430 mg (25%).

1H NMR (CDCl₃, 400 MHz): δ = 12.11 (s, 1H, OH), 9.92 (s, 1H, CHO), 7.71-7.70 (m, 2H, Ar-H), 1.44 (s, 9H, t-Bu); 13C NMR (CDCl₃, 100 MHz): δ = 196.7, 163.7, 140.0, 130.5 (3J(C,F) = 3 Hz), 129.4 (3J(C,F) = 4 Hz), 124.0 (1J(C,F) = 271 Hz), 121.8 (2J(C,F) = 33 Hz), 119.9, 35.3, 29.1. MS (ESI negative mode): m/z (%): 245.08 (100) [M+H]⁺.

(N,N'-bis(3-tert-Butyl-5-trifluoromethylsalicylidene))-trans-1,2-cyclohexanediame (H₂(Sal)CF₃):

To a solution of trans-1,2-cyclohexanediame (71 mg, 0.6 mmol) dissolved in MeOH (3 mL) was added 3-tert-butyl-5-trifluoromethyl-2-hydroxybenzaldehyde (305 mg, 1.24 mmol) in MeOH (3 mL). The reaction mixture was stirred at room temperature for 16 hours, during which time a light yellow precipitate formed. The solid was filtered and washed with cold MeOH. Yield: 330 mg (93%). 1H NMR (CDCl₃): δ = 8.30 (s, 2H, NCH), 7.44-7.45 (d, 2H, Ar-H, J = 2.0 Hz), 7.25-7.26 (d, 2H, Ar-H, J = 2.2 Hz), 3.35-3.42 (m, 2H, CH), 2.02-2.05 (m, 2H, CH₂), 1.88-1.96 (m, 2H, CH₂), 1.74–1.82 (m, 2H, CH₂), 1.45–1.55 (m, 2H, CH₂), 1.40 (s, 18H, t-Bu). 13C NMR (CDCl₃, 100 MHz): δ = 165.1, 163.2, 138.7, 127.0, (3J(C,F): 4 Hz), 126.2 (3J(C,F): 3 Hz), 124.5 (CF₃, 2J(C,F): 271 Hz), 120.0, 117.8, 72.3, 35.1, 32.9, 29.1, 24.3. MS (ESI): m/z (%): 571.27 (100) [H₂(Sal)CF₃ + H]⁺.
Elemental Analysis: calculated (%) for C$_{30}$H$_{36}$N$_2$O$_2$F$_6$: C 63.15, H 6.36, N 4.91; Found (%): C 63.50, H 6.53, N 5.12.

(N,N'-bis(3-tert-butyl-5-trifluoromethylsalicylidene))-trans-1,2-cyclohexanediamine Nickel (Ni(Sal)$_{\text{CF}3}$):

![Ni(Sal)$_{\text{CF}3}$](image)

To a solution of H$_2$(Sal)$_{\text{CF}3}$ (50 mg, 0.09 mmol) in Et$_2$O (2 mL), was added Ni(OAc)$_2$$\cdot$4 H$_2$O (22 mg, 0.09 mmol) in MeOH (2 mL). NEt$_3$ (25 µL, 0.18 mmol) was added, and the resulting solution was stirred at room temperature overnight during which time an orange precipitate appeared, which was collected by filtration and washed with cold methanol. The crude material was recrystallized in 1:1 CH$_2$Cl$_2$ : MeOH to afford orange crystals of Ni(Sal)$_{\text{CF}3}$. Yield: 22 mg (40%). MS (ESI): m/z (%): 627.20 (100) [Ni(Sal)$_{\text{CF}3}$$+$ H]$^+$.

Elemental Analysis: calculated (%) for C$_{30}$H$_{34}$N$_2$O$_2$F$_6$Ni: C 57.44, H 5.46, N 4.47; Found (%): C 57.82, H 5.19, N 4.54.

(N,N'-bis(3-tert-butyl-5-trifluoromethylsalicylidene))-trans-1,2-cyclohexanediamine Copper (Cu(Sal)$_{\text{CF}3}$):

![Cu(Sal)$_{\text{CF}3}$](image)
To a solution of $\text{H}_2(\text{Sal})^{\text{CF}_3}$ (100 mg, 0.18 mmol) in MeOH (2 mL), was added Cu(OAc)$_2$$\cdot$H$_2$O (35 mg, 0.18 mmol) in MeOH (2 mL). The resulting solution was stirred at room temperature overnight during which time a dark purple precipitate appeared, which was collected by filtration and washed with cold methanol. The crude material was recrystallized in 1:1 CH$_2$Cl$_2$ : MeOH to afford dark purple crystals. Yield: 60 mg (54%). MS (ESI): m/z (%): 632.19 (100) [Cu(\text{Sal})^{\text{CF}_3} + \text{H}]^+$. Elemental Analysis: calculated (%) for C$_{30}$H$_{34}$N$_2$O$_2$F$_6$Cu: C 57.00, H 5.42, N 4.43; Found (%): C 57.09, H 5.39, N 4.64.

3.3 Results and Discussion

3.3.1 Synthesis

The ligand $\text{H}_2(\text{Sal})^{\text{CF}_3}$ was synthesized by condensation of trans-1,2-cyclohexanediamine in the presence of two equivalents of 3-tert-butyl-5-trifluoromethyl-2-hydroxybenzaldehyde, which was prepared by the tert-butylation of the commercially available 4-trifluoromethylphenol, followed by a Duff formylation reaction. Ni(Sal)$_{\text{CF}_3}$ and Cu(Sal)$_{\text{CF}_3}$ were synthesized by reacting $\text{H}_2(\text{Sal})^{\text{CF}_3}$ with the corresponding metal acetate salts (Ni(OAc)$_2$$\cdot$4 H$_2$O and Cu(OAc)$_2$$\cdot$4 H$_2$O) under aerobic conditions. Two equivalents of NEt$_3$ were added to all metallation reactions. X-ray quality crystals of Ni(Sal)$_{\text{CF}_3}$, Cu(Sal)$_{\text{CF}_3}$ were grown by slow diffusion of MeOH into a concentrated CH$_2$Cl$_2$ solution of the compounds.
Scheme 3.1. Synthesis of $\text{H}_2\text{(Sal)}^{\text{CF}_3}$ and $\text{M(Sal)}^{\text{CF}_3}$.

Reaction conditions: (i) 9:1 tBuOH : MeOH, H$_2$SO$_4$; (ii) hexamethylenetetramine, CF$_3$COOH; (iii) 0.5 equiv. trans-1,2-cyclohexandiamine, MeOH; (iv) M(OAc)$_2$, MeOH, 2 eq. NEt$_3$.

3.3.2 Solid state X-ray structures

The molecular structures of $\text{Ni(Sal)}^{\text{CF}_3}$ and $\text{Cu(Sal)}^{\text{CF}_3}$ are presented in Figure 3.1 and Figure 3.2, respectively, and select crystallographic data shown in Table 3.1. Due to the high $R$-value (11.8) for the X-ray data of $\text{Ni(Sal)}^{\text{CF}_3}$ arising from a second disordered molecule of $\text{Ni(Sal)}^{\text{CF}_3}$ in the unit cell, the bond lengths could not be accurately determined. The solid state structures of the two compounds exhibit slightly distorted square planar geometries with the expected N$_2$O$_2$ coordination sphere from the ligand, with the distortion likely due to the sterically demanding ortho-tBu substituents. The C-O bond length of the phenolate is often used to evaluate the oxidation state of the ligand, and for the $\text{Cu(Sal)}^{\text{CF}_3}$ complex the C-O bond distances are consistent with a phenolate moiety, indicating the dianionic nature of the complex. The coordination bond distances are also in line with other $\text{Cu(Sal)}^R$ complexes.$^{26-27}$ Overall, the coordination sphere bond distances for both complexes were found to be slightly longer in comparison to other reported $\text{Cu(Sal)}^{\text{tBu}}$ derivatives, suggesting phenolates bearing the CF$_3$ moiety have lower donating ability in comparison to analogues with a tBu group. This is further illustrated by the shorter coordination bond distances for salen complexes.
with an electron-rich OMe para-ring substituent, in comparison to the derivative with a tBu moiety.\textsuperscript{26}

**Figure 3.1.** POV-Ray representation of Ni(Sal)\textsuperscript{CF3}.
Thermal ellipsoids at 50\% probability, hydrogen atoms excluded. The X-ray data for Ni(Sal)\textsuperscript{CF3} could not be fully solved and the structure is shown here for connectivity purposes.

**Figure 3.2.** POV-Ray representation of Cu(Sal)\textsuperscript{CF3}.
Table 3.1. Experimental coordination sphere metrical parameters for $\text{M(Sal)}^{\text{CF}_3}$ in comparison to other known $\text{M(Sal)}^R$ complexes in Å.

<table>
<thead>
<tr>
<th>Complex</th>
<th>M-O1</th>
<th>M-O2</th>
<th>M-N1</th>
<th>M-N2</th>
<th>C1-O1</th>
<th>C7-O2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(Sal)$^{\text{CF}_3}$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ni(Sal)$^{\text{tBu}_28}$</td>
<td>1.852</td>
<td>1.854</td>
<td>1.852</td>
<td>1.860</td>
<td>1.304</td>
<td>1.311</td>
</tr>
<tr>
<td>Ni(Sal)$^{\text{OMe}_26}$</td>
<td>1.839</td>
<td>1.839</td>
<td>1.832</td>
<td>1.832</td>
<td>1.324</td>
<td>1.324</td>
</tr>
<tr>
<td>Cu(Sal)$^{\text{CF}_3}$</td>
<td>1.901</td>
<td>1.895</td>
<td>1.938</td>
<td>1.939</td>
<td>1.295</td>
<td>1.297</td>
</tr>
<tr>
<td>Cu(Sal)$^{\text{tBu}_29}$</td>
<td>1.885</td>
<td>1.887</td>
<td>1.915</td>
<td>1.904</td>
<td>1.302</td>
<td>1.299</td>
</tr>
<tr>
<td>Cu(Sal)$^{\text{OMe}_26}$</td>
<td>1.884</td>
<td>1.884</td>
<td>1.922</td>
<td>1.922</td>
<td>1.314</td>
<td>1.314</td>
</tr>
</tbody>
</table>

3.3.3 Electrochemistry

Redox processes for $\text{M(Sal)}^{\text{CF}_3}$ were probed by cyclic voltammetry (CV) in CH$_2$Cl$_2$ by using tetra-$n$-butylammonium perchlorate ($^n$Bu$_4$NClO$_4$) as the supporting electrolyte. Two quasi-reversible one-electron oxidation waves are observed for Ni(Sal)$^{\text{CF}_3}$ as previously observed for other Ni(Sal)$^R$ complexes (Figure 3.3; Also see Section 2.3.2). The redox potentials versus Fc$^+$/Fc are in line with the electron-donating abilities of the para-ring substituents, which is reflected in the plot between first oxidation potential against Hammett constants ($\sigma_{\text{para}}$). A linear correlation ($R^2 = 0.974$), demonstrates that the oxidation potential is predominantly affected by the relative donating ability of the para-ring substituents (Figure 3.4). In addition, the difference between the first and second oxidation potentials ($\Delta E_{1/2}$) and comproportionation constant ($K_c$) of the one-electron oxidized complexes, calculated using Eq. 1, are also reported in Table 3.2, which provides insight regarding the degree of electronic coupling between the two redox-active phenolates in $[\text{Ni(Sal)}^{\text{CF}_3}]^{\text{2+}}$. The $\Delta E_{1/2}$ of the second oxidation wave, which was at the limit of the solvent window, could not be reliably determined using cyclic voltammetry. Thus, differential pulse voltammetry (DPV) was employed to determine the $\Delta E_{1/2}$, and subsequently $K_c$ values more accurately. Both $\Delta E_{1/2}$ and $K_c$ values for $[\text{Ni(Sal)}^{\text{CF}_3}]^{\text{2+}}$ suggest a delocalized electronic structure, which is further supported by theoretical analysis (See Section 3.3.5).
Table 3.2. Redox Potentials for Ni(Sal)\(^R\) versus Fc\(^+/\)Fc.\(^8\)

<table>
<thead>
<tr>
<th>Complex</th>
<th>(E_{1/2}^1) (V)</th>
<th>(E_{1/2}^2) (V)</th>
<th>(\Delta E_{1/2}^1) (V)</th>
<th>(K_c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(Sal)(^\text{NMe}_2) (^a)</td>
<td>-0.24 (0.14)</td>
<td>-0.08 (0.14)</td>
<td>0.16</td>
<td>2.9 x 10(^3)</td>
</tr>
<tr>
<td>Ni(Sal)(^\text{OMe}) (^a)</td>
<td>0.22 (0.14)</td>
<td>0.59 (0.14)</td>
<td>0.38</td>
<td>1.7 x 10(^8)</td>
</tr>
<tr>
<td>Ni(Sal)(^\text{tBu}) (^a)</td>
<td>0.37 (0.14)</td>
<td>0.85 (0.14)</td>
<td>0.48</td>
<td>2.6 x 10(^{10})</td>
</tr>
<tr>
<td>Ni(Sal)(^\text{CF}_3) (^b)</td>
<td>0.78 (0.13)</td>
<td>1.19 (0.17)</td>
<td>0.41</td>
<td>8.6 x 10(^6)</td>
</tr>
</tbody>
</table>

\(^a\) Cyclic voltammetry performed at 233 K. \(^b\) Cyclic voltammetry performed at 298 K. Peak-to-peak differences in brackets (\(|E_{pa} - E_{pc}|\) in V). Peak-to-peak difference for the Fc\(^+/\)Fc couple at 233 K is ca. 0.13 V, while at 298 K it is ca. 0.12 V.

\[ K_c = \exp \left( \frac{\Delta E_{1/2}^1 \cdot F}{RT} \right) \] (1)

Figure 3.3. Cyclic voltammogram (solid line) and differential pulse voltammogram (dotted line) of Ni(Sal)\(^\text{CF}_3\) in CH\(_2\)Cl\(_2\) at 298 K. Conditions: 1.5 mM complex, 0.1 M \(^\text{Bu}_4\text{NClO}_4\), scan rate 100 mV s\(^{-1}\).
Figure 3.4. Hammett plot of the first oxidation potential (V) of Ni(Sal)$^R$. $\sigma_{para}$ values from 32.

Two quasi-reversible one-electron oxidation waves were observed for Cu(Sal)$^{CF_3}$ (Figure 3.5). The redox processes for Cu(Sal)$^{CF_3}$ occur at considerably higher potentials in comparison to Cu(Sal)$^{tBu}$ and Cu(Sal)$^{OMe}$,26-27 as expected based on the trends observed for Ni(Sal)$^R$.30 Interestingly, it has been reported that the one-electron oxidation of Cu(Sal)$^{tBu}$ affords a Cu$^{III}$ species in the solid state, which is in equilibrium with a Cu$^{II}$-phenoxyl radical species in solution.33 The locus of oxidation is strongly dependent on temperature, highlighting the similarity in energy between the two electronic ground states. Conversely, the one-electron oxidation of the more electron rich OMe derivative Cu(Sal)$^{OMe}$ results in a Cu$^{II}$-phenoxyl radical species at all temperatures.26 Thus, the electron-withdrawing effect of the CF$_3$ moiety is expected to lower the energy of the ligand-based HOMO, thereby stabilizing the formation of a Cu$^{III}$ species. An additional irreversible reduction wave was observed at -2.06 V in the CV, similar reduction processes have been observed for other Cu$^{II}$-Schiff base complexes indicating reduction to their respective Cu$^I$ forms.34-36 Similar to the oxidation processes, the para-ring substituents in such salen systems can also tune the reduction potential of the Cu$^{II}$/Cu$^I$ process.36
Figure 3.5. Cyclic Voltammogram of Cu(Sal)\textsuperscript{CF3} in CH\textsubscript{2}Cl\textsubscript{2} at 298 K. Conditions: 1.5 mM complex, 0.1 M \textsuperscript{4}Bu\textsubscript{4}NClO\textsubscript{4}, scan rate 100 mV s\textsuperscript{-1}.

Table 3.3. Redox Potentials for Cu(Sal)\textsuperscript{R} versus Fc\textsuperscript{+}/Fc.\textsuperscript{6}

<table>
<thead>
<tr>
<th>Complex</th>
<th>(E_{\text{red}}) (V)</th>
<th>(E_{1/2}^{\text{i}}) (V)</th>
<th>(E_{1/2}^{\text{II}}) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(Sal)\textsubscript{OMe} \textsuperscript{26}</td>
<td>-</td>
<td>0.28</td>
<td>0.44</td>
</tr>
<tr>
<td>Cu(Sal)\textsubscript{tBu} \textsuperscript{27}</td>
<td>-</td>
<td>0.45</td>
<td>0.65</td>
</tr>
<tr>
<td>Cu(Sal)\textsubscript{CF3} \textsuperscript{CF3}</td>
<td>-2.06</td>
<td>0.74 (0.15)</td>
<td>1.23 (0.17)</td>
</tr>
</tbody>
</table>

Peak-to-peak differences in brackets (\(|E_{\text{pa}} - E_{\text{pc}}|\) in V). Peak-to-peak difference for the Fc\textsuperscript{+}/Fc couple at 298 K is ca. 0.12 V.

3.3.4 Electronic Spectroscopy

The electronic absorption spectra of Ni(Sal)\textsuperscript{CF3} is typical of low-spin d\textsuperscript{8} square-planar Ni\textsuperscript{II} bi-phenolate salen complexes (Figure 3.6).\textsuperscript{26,30} While no absorption was observed at energies lower than 20000 cm\textsuperscript{-1} for the neutral form, several intense NIR transitions were observed upon oxidation. These sharp and intense NIR bands for [Ni(Sal)\textsuperscript{CF3}]** are observed at similar energies to [Ni(Sal)\textsuperscript{tBu}]** (Table 3.4), and their band shapes were evaluated using the Hush equation (Eq. 2)\textsuperscript{37} to determine the extent of
delocalization in the resultant electronic structure. Indeed, the band shapes for both \([\text{Ni(Sal)}^{\text{Bu}}]^+\) and \([\text{Ni(Sal)}^{\text{CF3}}]^+\) were quite similar, suggesting that both oxidized species are Class III delocalized systems by the Robin-Day classification (See Section 2.1, Table 3.4).\(^{38}\) Taken together, the low energy NIR transition of \([\text{Ni(Sal)}^{\text{CF3}}]^+\) indicates that the ligand radical is delocalized over the ligand scaffold, similar to that reported for \([\text{Ni(Sal)}^{\text{Bu}}]^+\). While the stability of the oxidized species precluded its isolation for further crystallographic characterization (\(t_{1/2}\) (298 K): ca. 80 minutes), the delocalized electronic structure is supported by EPR data and DFT calculations (See Sections 3.3.5 and 3.3.6). Interestingly, while \([\text{Ni(Sal)}^{\text{Bu}}]^+\) and \([\text{Ni(Sal)}^{\text{CF3}}]^+\) both consist of delocalized electronic structures, the relative intensity of their respective NIR features differ (Table 3.4), and is further explored by TD-DFT calculations (See Section 3.3.7). The addition of 30 equivalents of pyridine to \([\text{Ni(Sal)}^{\text{CF3}}]^+\) in solution results in the loss of the NIR transitions and emergence of a new transition at 20300 cm\(^{-1}\) (Figure 3.6). This spectral pattern has been previously observed for the axial binding of two pyridines to \([\text{Ni(Sal)}^{\text{Bu}}]^+\) to form \([\text{Ni}^{\text{III}}(\text{Sal})^{\text{Bu}}(\text{py})_2]^+\), arising from a shift in the locus of oxidation from the ligand to metal.\(^{39}\) The formation of \([\text{Ni(Sal)}^{\text{CF3}}]^+\) and \([\text{Ni}^{\text{III}}(\text{Sal})^{\text{CF3}}(\text{py})_2]^+\) is further evidenced by EPR spectroscopy (See Section 3.3.5).

\[
\Delta v_{1/2} = \sqrt{\frac{16 \ln 2}{RT}} v_{1/2,\text{ax}} \tag{2}
\]
Figure 3.6. UV-Vis-NIR spectrum of $\text{Ni(Sal)}^{\text{CF}_3}$ (black), $[\text{Ni(Sal)}^{\text{CF}_3}]^{2+}$ (red) and $[\text{Ni}^{\text{III}}\text{(Sal)}^{\text{CF}_3}\text{(py)}_2]^+$ (blue) at 0.4 mM in CH$_2$Cl$_2$ at 198 K. Intermediate gray lines measured during the oxidation titration with $[\text{Ni(C_6H_3Br_2)}_3]^{2+}[\text{SbF}_6]^{-}$. Vertical green bars indicates the energy of the calculated NIR transitions for $[\text{Ni(Sal)}^{\text{CF}_3}]^{2+}$.

Table 3.4. Observed NIR transitions, experimental $\Delta \nu_{1/2}$, and calculated $\Delta \nu_{1/2}$ based on the Hush equation for $[\text{Ni(Sal)}^{\text{Bu}}]^{2+}$ and $[\text{Ni(Sal)}^{\text{CF}_3}]^{2+}$.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\nu_{\text{max}}$ (cm$^{-1}$)</th>
<th>$\epsilon$ (M$^{-1}$ cm$^{-1}$)</th>
<th>Experimental $\Delta \nu_{1/2}$ (cm$^{-1}$)</th>
<th>Calculated $\Delta \nu_{1/2}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Ni(Sal)}^{\text{Bu}}]^{2+}$</td>
<td>4700</td>
<td>21600</td>
<td>660</td>
<td>2700</td>
</tr>
<tr>
<td></td>
<td>9200</td>
<td>5600</td>
<td>840</td>
<td>3700</td>
</tr>
<tr>
<td>$[\text{Ni(Sal)}^{\text{CF}_3}]^{2+}$</td>
<td>4900</td>
<td>16600</td>
<td>770</td>
<td>2700</td>
</tr>
<tr>
<td></td>
<td>8600</td>
<td>13100</td>
<td>760</td>
<td>3600</td>
</tr>
</tbody>
</table>

The electronic absorption spectra of $\text{Cu(Sal)}^{\text{CF}_3}$ is typical of low-spin $d^9$ square-planar Cu$^{II}$ bis-phenolate salen complexes, with an intense charge transfer transition at 28000 cm$^{-1}$ ($\epsilon = 12500$ M$^{-1}$ cm$^{-1}$) and a weak d-d transition at 17600 cm$^{-1}$ ($\epsilon = 600$ M$^{-1}$ cm$^{-1}$) (Figure 3.7).$^{26,33}$ The oxidation of $\text{Cu(Sal)}^{\text{CF}_3}$ leads to the appearance of two new bands at 18700 cm$^{-1}$ ($\epsilon = 15000$ M$^{-1}$ cm$^{-1}$) and 5800 cm$^{-1}$ ($\epsilon = 1500$ M$^{-1}$ cm$^{-1}$), which are consistent with previous reports.$^{33}$ The emergence of the intense band at ca. 18000 cm$^{-1}$ has been linked to the formation of a Cu$^{III}$ species, as observed for $[\text{Cu(Sal)}^{\text{Bu}}]^+$ at low
temperature ($\varepsilon = 14000 \text{ M}^{-1} \text{cm}^{-1}$). In comparison, no such band was observed for [Cu(Sal)$^{\text{OMe}}$]$^+$, where the formation of a Cu$^{\text{II}}$-phenoxy radical species is favored due to the electron-donating ability of the para-OMe moiety. In addition, the intensity of the band at ca. 18000 cm$^{-1}$ for [Cu(Sal)$^{\text{tBu}}$]$^+$ is reduced by 50% upon warming from 198 K to 298 K, signifying a temperature-dependent equilibrium between a Cu$^{\text{III}}$-phenolate species at low temperature and a Cu$^{\text{II}}$-phenoxy radical species at room temperature. This effect was far less pronounced for [Cu(Sal)$^{\text{CF3}}$]$^+$ ($\varepsilon_{198K} = 15000 \text{ M}^{-1} \text{cm}^{-1}$, $\varepsilon_{298K} = 12000 \text{ M}^{-1} \text{cm}^{-1}$, Figure 3.8). This suggests the formation of a Cu$^{\text{III}}$-phenolate species upon oxidation is more favorable, likely due to the CF$_3$ moiety decreasing the energy of a ligand-based HOMO.

![Figure 3.7](image)

**Figure 3.7.** UV-Vis-NIR spectrum of Cu(Sal)$^{\text{CF3}}$ (black) and [Cu(Sal)$^{\text{CF3}}$]$^+$ (red) at 0.4 mM in CH$_2$Cl$_2$ at 198 K. Intermediate gray lines measured during the oxidation titration with [N(C$_6$H$_5$Br$_2$)$_3$]$^+$[SbF$_6$]$^-$. 
3.3.5 Continuous Wave Electron Paramagnetic Resonance

The X-band EPR spectrum of $[\text{Ni(Sal)}^{\text{CF}_3}]^{**}$ collected at 195 K in CH$_2$Cl$_2$ showed a broad isotropic signal at $g_{\text{iso}} = 2.067$ (Figure 3.9 and Table 3.5). A minor signal at $g = 2.003$ is assigned to an organic decomposition product, as it comprises only 3% of the overall signal by spin integration. Due to solvent effects, collection of this spectrum was performed in a capillary tube with a much smaller sample volume, resulting in decreased signal strength. The observed $g$-value is in line with the predicted metal contribution to the SOMO by DFT calculations when compared to other $[\text{Ni(Sal)}^R]^**$ complexes (See Table 2.5 in Chapter 2). Interestingly, a rhombic spectrum made up of two components with $g_{\text{av}}$ of ca. 2.18 was observed when the sample was frozen (20 K), indicating the formation of two distinct Ni$^{\text{III}}$ species (Figure 3.9). This likely arises from the axial ligation of a donor species (D, possibly from oxidation reaction by-product N(C$_6$H$_3$Br$_2$)$_3$, the SbF$_6^-$ counterion, or adventitious H$_2$O from sample preparation) in solution, as the $g_{\text{av}}$ value suggests a shift in the locus of oxidation from ligand to metal to generate a $[\text{Ni}^{\text{III}}(\text{Sal})^{\text{CF}_3}(D)_2]^**$ species. In contrast, the EPR spectrum of $[\text{Ni(Sal)}^{\text{tBu}}]^**$ exhibits a rhombic signal ($g_1 = 2.063$, $g_2 = 2.013$, $g_3 = 1.988$, $g_{\text{av}} = 2.021$) under the same experimental conditions, indicating that $[\text{Ni(Sal)}^{\text{tBu}}]^**$ maintains ligand radical character.
upon freezing, with the slight rhombicity attributed to weak axial interactions.\textsuperscript{31} Additionally, a low spin $S = 1/2$ Ni\textsuperscript{III} center coordinated in a square planar geometry typically displays a rhombic EPR signal at $g_{av}$ values ca. 2.12 – 2.17, which is similar to the $g_{av}$ of a frozen solution of [Ni(Sal)$^{CF_3}$]$^{**}.\textsuperscript{40-43}$ Thus it is possible that a square planar [Ni\textsuperscript{III}(Sal)$^{CF_3}$]$^+$ complex forms upon freezing, or that a mixture of square planar and octahedral Ni\textsuperscript{III} species exist in frozen CH$_2$Cl$_2$. The shift in the locus of oxidation observed for [Ni(Sal)$^{CF_3}$]$^{**}$ upon freezing truly highlights the electron-deficient nature of the nickel center. As expected, the addition of 30 equivalents of pyridine results in a rhombic spectrum, which has been previously observed in the formation of [Ni\textsuperscript{III}(Sal)$^{tBu}(py)_2$]$^+$ (Figure 3.9).\textsuperscript{39} In addition, hyperfine coupling to the two nitrogen nuclei from the pyridine moieties was observed.
Figure 3.9. X-band EPR spectra for: (a) \([\text{Ni(Sal)}^{\text{CF}_3}]^{++}\) at 195 K; (b) \([\text{Ni(Sal)}^{\text{CF}_3}]^{++}\) at 20 K and (c) \([\text{Ni}^{\text{IIl}}(\text{Sal})^{\text{CF}_3}(\text{py})_2]^{++}\) at 20 K in \(\text{CH}_2\text{Cl}_2\).

Experimental spectrum: black, Simulations: red; Species 1 and 2: blue dotted lines. Conditions: Frequency: (a) 9.386 GHz, (b) 9.383 GHz and (c) 9.380 GHz; Power: 2.0 mW; modulation frequency: 100 kHz; amplitude 0.6 mT.

Table 3.5. X-band EPR simulation parameters for the Ni complex.

<table>
<thead>
<tr>
<th>Complex</th>
<th>(g_x)</th>
<th>(g_y)</th>
<th>(g_z)</th>
<th>(g_{av})</th>
<th>(A_z) (MHz)</th>
<th>Contribution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Ni(Sal)}^{\text{CF}_3}]^{++}), 195 K (^a)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.067</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>([\text{Ni(Sal)}^{\text{CF}_3}]^{++}), 20 K, (S_1) (^b)</td>
<td>2.328</td>
<td>2.247</td>
<td>2.001</td>
<td>2.192</td>
<td>-</td>
<td>50</td>
</tr>
<tr>
<td>([\text{Ni(Sal)}^{\text{CF}_3}]^{++}), 20 K, (S_2) (^b)</td>
<td>2.291</td>
<td>2.234</td>
<td>2.020</td>
<td>2.182</td>
<td>-</td>
<td>50</td>
</tr>
<tr>
<td>([\text{Ni(Sal)}^{\text{CF}_3}(\text{py})_2]^{++}), 20 K (^b)</td>
<td>2.209</td>
<td>2.171</td>
<td>2.025</td>
<td>2.135</td>
<td>63</td>
<td>-</td>
</tr>
</tbody>
</table>

\(S_1 = \) Species 1; \(S_2 = \) Species 2; \(^a\) Collection in capillary tube; \(^b\) Collection in 4 mm outer-diameter EPR tube.
The X-band EPR spectrum of \( \text{Cu(Sal)}^{\text{CF}_3} \) collected at 20 K exhibited features consistent with a square planar \( d^9 \) Cu\(^{\text{II}} \) center as observed for other \( \text{Cu(Sal)}^R \) complexes (Figure 3.10, Table 3.6).\(^{26-27} \) Oxidation of \( \text{Cu(Sal)}^{\text{CF}_3} \) to \( [\text{Cu(Sal)}^{\text{CF}_3}]^+ \) results in a substantial decrease in the EPR signal to < 10% of the original intensity by spin integration, which supports the formation of a Cu\(^{\text{III}} \) species over a Cu\(^{\text{II}}\)-phenoxyl radical species. This is in line with results from the UV-Vis data (See Section 3.3.4).

![Figure 3.10](image)

**Table 3.6.** X-band EPR simulation parameters for \( \text{Cu(Sal)}^{\text{CF}_3} \).

<table>
<thead>
<tr>
<th>Complex</th>
<th>( g_\parallel )</th>
<th>( g_\perp )</th>
<th>( A_{\text{Cu},\parallel} ) (MHz)</th>
<th>( A_{\text{Cu},\perp} ) (MHz)</th>
<th>( A_{\text{N},\parallel} ) (MHz)</th>
<th>( A_{\text{N},\perp} ) (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Cu(Sal)}^{\text{CF}_3}, 20 \text{ K} ) (^a)</td>
<td>2.193</td>
<td>2.046</td>
<td>575</td>
<td>85</td>
<td>30</td>
<td>40</td>
</tr>
</tbody>
</table>

\(^a\) Collection in 4 mm outer-diameter EPR tube
3.3.6 Theoretical Characterization

A symmetric structure was predicted for Ni(Sal)$_{\text{CF3}}$ using the B3LYP functional with a polarized continuum model (PCM) for CH$_2$Cl$_2$ (Table 3.7). A symmetric structure was also predicted for [Ni(Sal)$_{\text{CF3}}$]$^{2+}$ using the B3LYP method, with a contraction in the coordination sphere in comparison to Ni(Sal)$_{\text{CF3}}$ (Table 3.7). Importantly, using the CAM-B3LYP functional, which was used in Chapter 2 to more accurately predict the asymmetric geometric and electronic structure for certain [Ni(Sal)$_{\text{R}}$]$^{2+}$ complexes (See Section 2.3.3), also results in a symmetric structure. A delocalized electronic structure was predicted for [Ni(Sal)$_{\text{CF3}}$]$^{2+}$ using both methods (Figure 3.11), which is supported by the formation of sharp and intense NIR bands in the UV-Vis-NIR experiment (See Section 3.3.4), which is diagnostic for the formation a symmetric electronic structure. Interestingly, the amount of spin density located on the nickel center for [Ni(Sal)$_{\text{CF3}}$]$^{2+}$ (SD$_{\text{Ni}}$: 34%) is significantly higher in comparison to other [Ni(Sal)$_{\text{R}}$]$^{2+}$ complexes ([Ni(Sal)$_{\text{tBu}}$]$^{2+}$: SD$_{\text{Ni}}$: 21%; [Ni(Sal)$_{\text{OMe}}$]$^{2+}$: SD$_{\text{Ni}}$: 12%; [Ni(Sal)$_{\text{NMe2}}$]$^{2+}$: SD$_{\text{Ni}}$: 5%), indicating a higher degree of metal contribution to the SOMO of the complex. This observation follows the trends established previously for other [Ni(Sal)$_{\text{R}}$]$^{2+}$ complexes, where electron-donating para-ring substituents result in a decreased metal contribution to the SOMO, as observed in the EPR spectra for [Ni(Sal)$_{\text{CF3}}$]$^{2+}$ (See Section 3.3.5).

Table 3.7. Calculated coordination sphere metrical parameters for Ni(Sal)$_{\text{CF3}}$ and [Ni(Sal)$_{\text{CF3}}$]$^{2+}$ in Å.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Ni-O1</th>
<th>Ni-O2</th>
<th>Ni-N1</th>
<th>Ni-N2</th>
<th>C-O1</th>
<th>C-O2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(Sal)$_{\text{CF3}}$</td>
<td>1.854</td>
<td>1.854</td>
<td>1.847</td>
<td>1.847</td>
<td>1.301</td>
<td>1.301</td>
</tr>
<tr>
<td>[Ni(Sal)$_{\text{CF3}}$]$^{2+}$</td>
<td>1.795</td>
<td>1.795</td>
<td>1.828</td>
<td>1.828</td>
<td>1.302</td>
<td>1.302</td>
</tr>
</tbody>
</table>
Figure 3.11. Calculated spin density of $[\text{Ni(Sal)}^{\text{CF}_3}]^+$ using the B3LYP functional and a polarized continuum model for CH$_2$Cl$_2$.

A symmetric structure was predicted for Cu(Sal)$_{\text{CF}_3}$ within $\pm$ 0.01 Å of the experimental values using the B3LYP functional with a polarized continuum model (PCM) for CH$_2$Cl$_2$, a method that has been previously used for other Cu(Sal)$_R$ complexes (Table 3.8).$^{33}$ In line with solution phase magnetic data, the spin density of Cu(Sal)$_{\text{CF}_3}$ shows spin-covalency between the Cu $d_{x^2-y^2}$ orbital and the coordinating atoms, as expected for a d$^9$ metal complex (Figure 3.12).

Table 3.8. Experimental and calculated coordination sphere metrical parameters for Cu(Sal)$_{\text{CF}_3}$ and $[\text{Cu(Sal)}^{\text{CF}_3}]^+$ in Å.

<table>
<thead>
<tr>
<th>Complex</th>
<th>M-O1</th>
<th>M-O2</th>
<th>M-N1</th>
<th>M-N2</th>
<th>C-O1</th>
<th>C-O2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(Sal)$_{\text{CF}_3}$, Experimental</td>
<td>1.901(4)</td>
<td>1.894(7)</td>
<td>1.938(1)</td>
<td>1.939(2)</td>
<td>1.295(0)</td>
<td>1.297(4)</td>
</tr>
<tr>
<td>Cu(Sal)$_{\text{CF}_3}$, Calculated</td>
<td>1.905</td>
<td>1.905</td>
<td>1.931</td>
<td>1.931</td>
<td>1.299</td>
<td>1.299</td>
</tr>
<tr>
<td>$[\text{Cu(Sal)}^{\text{CF}_3}]^+$, S = 0</td>
<td>1.835</td>
<td>1.836</td>
<td>1.861</td>
<td>1.861</td>
<td>1.315</td>
<td>1.315</td>
</tr>
<tr>
<td>$[\text{Cu(Sal)}^{\text{CF}_3}]^+$, S = 1</td>
<td>1.899</td>
<td>1.899</td>
<td>1.924</td>
<td>1.924</td>
<td>1.288</td>
<td>1.288</td>
</tr>
</tbody>
</table>
The oxidation of Cu(Sal)\textsuperscript{CF3} can afford one of three electronic states: (i) a d\textsuperscript{8} Cu\textsuperscript{III}-salen complex (S = 0), (ii) a Cu\textsuperscript{II} complex antiferromagnetically-coupled to a phenoxy radical (broken symmetry, S = 0), or (iii) a Cu\textsuperscript{II} complex ferromagnetically-coupled to a phenoxy radical (S = 1). All three possibilities were explored by DFT calculations, with the broken symmetry optimization converging to the singlet solution. This was observed for calculations of [Cu(Sal)\textsuperscript{tBu}]\textsuperscript{+} under the same theoretical parameters.\textsuperscript{33} In this case the S = 1 solution for [Cu(Sal)\textsuperscript{CF3}]\textsuperscript{+} was predicted to be lowest in energy by 2.7 kcal/mol, which is in contrast with the UV-Vis-NIR data, and likely reflects the propensity of DFT calculations to favor delocalized electronic structures.\textsuperscript{44} At the same level of theory, the S = 1 solution of [Cu(Sal)\textsuperscript{tBu}]\textsuperscript{+} is also incorrectly predicted to be lower in energy by 2.5 kcal/mol.\textsuperscript{33} The small energy difference between the two states is in line with the variable temperature UV-Vis experiment for [Cu(Sal)\textsuperscript{CF3}]\textsuperscript{+} (See Section 3.3.4), demonstrating the locus of oxidation is only slightly temperature dependant. While the intensity of the band at ca. 18000 cm\textsuperscript{-1} for [Cu(Sal)\textsuperscript{tBu}]\textsuperscript{+} is reduced by ca. 50% with increased temperature, the same increase in temperature only led to a ca. 20% decrease in intensity for [Cu(Sal)\textsuperscript{CF3}]\textsuperscript{+}. Taken together, these results suggests that the formation of a Cu\textsuperscript{III} species is more favorable for [Cu(Sal)\textsuperscript{CF3}]\textsuperscript{+} in comparison to [Cu(Sal)\textsuperscript{tBu}]\textsuperscript{+}. The preparation of a concentrated bulk solution of [Cu(Sal)\textsuperscript{CF3}]\textsuperscript{+} for solution magnetic analysis has proven extremely challenging due to the high oxidation potential and limited stability of the oxidized species.
3.3.7 Theoretical Analysis of the NIR transitions for [Ni(Sal)\text{CF}_3]^{++}

Time-Dependant Density Functional Theory (DFT) calculations\textsuperscript{19-20} were undertaken to gain insight into the spectral features of [Ni(Sal)\text{CF}_3]^{++}. As discussed in Chapter 2, calculations employing the CAM-B3LYP functional satisfactorily reproduce the NIR transitions observed experimentally for [Ni(Sal)\text{R}]^{++} (See Section 2.3.3). Indeed, the CAM-B3LYP functional also accurately predicts the appearance of two NIR transitions for [Ni(Sal)\text{CF}_3]^{++}. Interestingly, the same NIR bands were predicted when using the B3LYP functional with a solvent model for CH\textsubscript{2}Cl\textsubscript{2} for [Ni(Sal)\text{tBu}]^{++} and [Ni(Sal)\text{CF}_3]^{++}, and these results are presented herein (Figure 3.13). While the higher energy NIR transition for [Ni(Sal)\text{tBu}]^{++} (E = 10400 cm\textsuperscript{-1}, f = 0.0874) is predicted to be significantly less intense in comparison to the lower energy band (E = 5500 cm\textsuperscript{-1}, f = 0.1723), this trend is reversed for [Ni(Sal)\text{CF}_3]^{++} (E = 9300 cm\textsuperscript{-1}, f = 0.1248; E = 5700 cm\textsuperscript{-1}, f = 0.0717). The experimental spectrum for [Ni(Sal)\text{tBu}]^{++} and [Ni(Sal)\text{CF}_3]^{++} showed NIR bands of similar intensities (Figures 2.13 and 3.6, Table 3.8). Analysis of the orbitals involved in both predicted bands for [Ni(Sal)\text{CF}_3]^{++} reveals significant ligand to metal charge transfer character (Figure 3.13), which is in contrast to the other [Ni(Sal)\text{R}]^{++} species discussed in Chapter 2.

These data suggest that the \textit{para}-ring electron-withdrawing group serves to increase the charge density on the metal center, which is also reflected in the spin density on the metal center. As such, these NIR bands may be unique spectroscopic handles to probe the degree of metal participation in the electronic structure of [Ni(Sal)\text{R}]^{++} and other structurally similar compounds, and deserves further attention. Nevertheless, the intense NIR bands for [Ni(Sal)\text{CF}_3]^{++} originates from symmetric orbitals that are mainly centered on the ligand framework, as previously reported for [Ni(Sal)\text{tBu}]^{++}. Based on these calculations, which are supported by experimental data, [Ni(Sal)\text{CF}_3]^{++} is predicted to be a Class III intervalence compound.
Table 3.9. Observed NIR transitions and their theoretical analysis for $[\text{Ni(Sal)}^{\text{tBu}}]^+$ and $[\text{Ni(Sal)}^{\text{CF3}}]^+$.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\nu_{\text{max}}$ (cm$^{-1}$)</th>
<th>$\varepsilon$ (M$^{-1}$ cm$^{-1}$)</th>
<th>Predicted $\nu_{\text{max}}$ (cm$^{-1}$)</th>
<th>Predicted Oscillator strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Ni(Sal)}^{\text{tBu}}]^+$</td>
<td>4700</td>
<td>21600</td>
<td>5500</td>
<td>0.1723</td>
</tr>
<tr>
<td></td>
<td>9200</td>
<td>5600</td>
<td>10400</td>
<td>0.0874</td>
</tr>
<tr>
<td>$[\text{Ni(Sal)}^{\text{CF3}}]^+$</td>
<td>4900</td>
<td>16600</td>
<td>5700</td>
<td>0.0717</td>
</tr>
<tr>
<td></td>
<td>8600</td>
<td>13100</td>
<td>9300</td>
<td>0.1248</td>
</tr>
</tbody>
</table>

Figure 3.13. Kohn Sham Molecular Orbitals associated with the predicted NIR transitions by TD-DFT calculations using the B3LYP functional with a polarized continuum model (PCM) for CH$_2$Cl$_2$ for (a) $[\text{Ni(Sal)}^{\text{tBu}}]^+$ and (b) $[\text{Ni(Sal)}^{\text{CF3}}]^+$.

3.4 Conclusion

Nickel and copper complexes of an electron-deficient salen ligand H$_2$Sal$^{\text{CF3}}$ were prepared. The electrochemistry of both complexes displayed quasi-reversible redox waves at higher potentials in comparison to their $M(\text{Sal})^R$ counterparts, in line with the electron-withdrawing nature of the para-ring substituents. Chemical oxidation,
monitored by UV-Vis-NIR spectroscopy, afforded the corresponding [Ni(Sal)\text{CF}_3]^{2+} and [Cu(Sal)\text{CF}_3]^{2+} species. The locus of oxidation was demonstrated to be ligand-based for [Ni(Sal)\text{CF}_3]^{2+} by sharp NIR transitions in the UV-Vis-NIR spectrum, and a broad isotropic signal at \(g = 2.067\) by EPR spectroscopy. The sharp NIR transitions observed for [Ni(Sal)\text{CF}_3]^{2+} are indicative of a delocalized electronic structure, which is further supported by electrochemical data and theoretical methods. In addition, the increased metal character for [Ni(Sal)\text{CF}_3]^{2+}, which is evident in the shift in \(g\)-value observed in the EPR spectrum, was well predicted. In the case of [Cu(Sal)\text{CF}_3]^{2+}, a strong absorption band at 18700 cm\(^{-1}\) in the UV-Vis-NIR spectrum suggests the formation of a Cu\text{III} species. This band is much less dependent on temperature in comparison to [Cu(Sal)\text{tBu}]^{2+}, which exists as an equilibrium between a Cu\text{III} complex and a Cu\text{II} ligand radical in solution. Taken together, these results show that the electron-deficient salen ligand \text{H}_2\text{Sal}\text{CF}_3 is capable of stabilizing higher metal oxidation states, and is of further interest in catalyst design. For future directions, see Chapter 6.

3.5 References


23. Gorelsky, S. I. AOMix, Program for Molecular Orbital Analysis.


Chapter 4. Tuning Ligand Electronics by Peripheral Substitution on Cobalt Salen Complexes: Structure and Polymerization Activity

Adapted from: Chiang, L.¹, Allen, L. E. N.², Alcantara, J.¹, Wang, M. C. P.¹, Storr, T.¹, and Shaver, M. P.², Dalton Trans., 2014, 43, 4295-4304.

¹Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada.

²School of Chemistry, University of Edinburgh, Edinburgh, United Kingdom.

LC performed the synthesis, electrochemistry, continuous wave EPR experiments and theoretical calculations with assistance from JA. LENA performed the polymerization studies. MCPW collected the XPS data.

4.1 Introduction

Due to their relative ease of synthesis and ability to form stable complexes with many metals in a variety of oxidation states, salen ligands have been extensively explored as catalysts for organic transformations.¹-⁹ The modular synthesis of the salen framework allows for easy tuning of both sterics and electronics, providing a means to study how subtle changes to the ligand framework influences reactivity. In many cases the steric and electronic properties of the salen ligand exerts a profound effect on the reaction outcome. For example, enantiomeric excess (ee) values for the Mn-salen catalyzed asymmetric epoxidation of pro-chiral olefins depends on the nature of the chiral diimine bridge and the identity of the ortho- and para-ring substituents.²,¹⁰-¹² While the ortho-ring substituents primarily provide steric bulk to influence substrate approach, the electron donating ability of the para-ring substituents has a significant effect on the reaction outcome by altering the position of the transition state along the reaction
In the case of Mn-salen complexes, electron donating \textit{para}-ring substituents lead to a late transition state, affording the highest ee values. A smaller effect by the \textit{para}-ring substituents (Br, H, tBu) is observed for Co-salen mediated copolymerization of propylene oxide and CO$_2$, with the tBu derivative showing the highest regioselectivity.\textsuperscript{13} Similar to the Mn-salen results, electron donating substituents increases the rate of copolymer formation for Cr-salen catalyzed cyclohexene oxide / CO$_2$ copolymerization.\textsuperscript{5,14} These results highlight the role of the electron donating ability of the \textit{para}-ring substiuents on the catalytic activity of the metal center. The electronic structure and polymerization activity of a series of Co salen complexes where the electron donating ability of the \textit{para}-ring substituents (NMe$_2$ > OMe > tBu > NO$_2$) was varied will be discussed in this chapter (Figure 4.1).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{structures.png}
\caption{Structures of Co$^{II}$-salen complexes (Co(Sal)$^R$).}
\end{figure}

The role these Co complexes play in controlling organometallic mediated radical polymerization (OMRP) is of interest.\textsuperscript{15} In this variant of controlled radical polymerization, the fast and reversible homolytic cleavage of a metal-carbon bond is exploited to limit radical concentrations and control the properties of the polymer products. OMRP may proceed through one of two pathways: Reversible termination (RT-OMRP, Scheme 4.1) or degenerative transfer (DT-OMRP, Scheme 4.2). In RT-OMRP, the radical terminated polymeric chain, generated by a monomer reacting with a conventional free radical initiator, reacts with a redox-active metal center to form a metal-carbon bond, resulting in a metal-terminated dormant species (Scheme 4.1, pathway (i)). This dormant species is in equilibrium with the starting materials, with the equilibrium favoring the dormant species such that only a low concentration of radical
terminated chains is in solution, which is crucial as it allows for control in the overall length (i.e. molecular weight) and uniformity (i.e. polydispersity index (PDI)) of the polymers formed. Once released from the metal center, the radical terminated chains can undergo propagation with other monomers in solution (Scheme 4.1, pathway (ii)) until the growing radical terminated polymer chain reacts with the metal complex to form a dormant species (Scheme 4.1, pathway (iii)). The reaction can be terminated by the addition of protic solvents.

Scheme 4.1. Reversible Termination OMRP (RT-OMRP) mechanism.

OMRP can also proceed through a degenerative transfer process (DT-OMRP, Scheme 4.2). In this case, the formation of the initial dormant species is not reversible, implying that polymerization does not occur until the metal complex has been converted to the corresponding organometallic dormant species, which is reflected in the characteristically long induction periods for DT-OMRP. At this point, radical terminated chains can undergo propagation (Scheme 4.2, pathway (ii)), followed by an associative exchange between the propagating radical chain with the dormant species (Scheme 4.2, pathway (iii)). This displaces the initial radical that was bound to the metal, which then re-enters the catalytic cycle. The dormant species can be hydrolyzed by the addition of protic solvents in a similar manner to RT-OMRP. Central to both methodologies is the strength of the metal-carbon bond, which dictates the reactivity and reaction pathway of the organometallic species. This can be tuned through the choice of metal as well as by ligand design (steric and/or electronic effects) to promote the controlled polymerization of a large array of monomers.15
Scheme 4.2. Degenerative transfer OMRP (DT-OMRP) mechanism.

Cobalt complexes dominate the OMRP literature \(^{16}\), imparting the best control, although the development of other metals as OMRP mediators is a recent topic of interest. \(^{15,17-21}\) Early cobalt OMRP catalysts were based on nitrogen donors and examples are shown in Figure 4.2. Complexes of porphyrins are particularly efficient for the OMRP of acrylates. \(^{22-25}\) A more recent report examined a series of 1,3-bis(2-pyridylimino)isoindolate ligands, structurally related to porphyrins, but lacking a fourth N-donor. \(^{26}\) These complexes were active for acrylate polymerization, but did not show the anticipated structure-activity relationship. The authors concluded that the cobalt-carbon bond was decoupled from the ligand substituents, so inclusion of electron withdrawing or electron donating groups had no effect on the polymerization behavior. Cobalt species incorporating oxygen donors, such as bis-acetylacetonate Co\(^{II}\) and related complexes \(^{15-18}\), are very efficient for the OMRP of vinyl acetate \(^{27-32}\) and careful choice of reaction conditions has allowed expansion of the monomer scope to include acrylates \(^{33-35}\), acrylonitrile \(^{36-39}\), other vinyl ester monomers \(^{40-41}\) and N-vinylpyrrolidone. \(^{40,42}\) The use of mixed N,O-donor systems in cobalt-mediated OMRP is limited to reports on the β-ketoiminates \(^{43-44}\), which exert reasonable control over methyl acrylate and vinyl acetate polymerization, and a recent report on the highly efficient degenerative transfer OMRP of vinyl acetate and methyl acrylate mediated by Co\(^{II}\) \([N,N\text{-bis}(3,5-di\text{-}tert\text{-}butyl)salicylidene]-1,2\text{-cyclohexanediamine}\) \((\text{Co(Sal})_{Bu})^{45}\), was reported during the course of this research.
In this Chapter, the electronic structures of a series of Co$^{II}$ salen complexes with varying para-ring substituents were investigated. The ortho-ring positions are tert-butyl protected to maintain the geometry at the metal center. The para-ring substituents were found to influence both the electron density at the metal center as well as the overall reactivity via increasing stability of the Co$^{II}$ forms in the order of NMe$_2$ > OMe > tBu > NO$_2$. The more electron donating substituents should thus increase the concentration of propagating radicals in the system and the use of the Co$^{II}$ salen complexes in reversible termination RT-OMRP was evaluated.

4.2 Experimental

4.2.1 Materials

All chemicals used were of the highest grade available and were further purified whenever necessary. Literature methods were followed to prepare Schiff-base
ligands\(^{47-51}\) \(\text{H}_2(\text{Sal})^{\text{NO}_2}\), \(\text{H}_2(\text{Sal})^{\text{tBu}}\), \(\text{H}_2(\text{Sal})^{\text{OMe}}\), \(\text{H}_2(\text{Sal})^{\text{NMe}_2}\), and Co complexes\(^{47,50,52}\) \(\text{Co}(\text{Sal})^{\text{tBu}}\), \(\text{Co}(\text{Sal})^{\text{OMe}}\). Monomers styrene, methyl methacrylate, methyl acrylate and vinyl acetate were purchased from Aldrich Chemical Co. and dried by stirring over calcium hydride for 24 hours, before being vacuum transferred, degassed and stored at -35°C under inert atmosphere. Azo\(\text{bis}(\text{isobutyronitrile}), \text{AIBN}, \) was purchased from Aldrich, recrystallized from methanol prior to use and then stored at -35°C under inert atmosphere. \(\text{V-70}\) was purchased from Wako and used as received.

4.2.2 Instrumentation

\(^1\text{H}\) NMR were recorded at 298 K with a Bruker Avance Spectrometer (300 MHz) in CDCl\(_3\). Cyclic voltammetry (CV) was performed using a PAR-263A potentiometer, equipped with a Ag wire reference electrode, a platinum disk working electrode, and a Pt counter electrode with 0.1 M \(^4\text{Bu}_4\text{NClO}_4\) solutions in CH\(_2\)Cl\(_2\). Decamethylferrocene was used as an internal standard, and redox processes assigned to the Co complexes were directly referenced to the standard.\(^{53}\) Mass spectra (positive ion) were obtained on an Agilent 6210 TOF ESI-MS instrument. All EPR spectra were collected using a Bruker EMXplus spectrometer operating with a premiumX X-band (~9.5 GHz) microwave bridge. Low temperature measurements of frozen solutions used a Bruker helium temperature-control system and a continuous flow cryostat. Samples for X-band measurements were placed in 4 mm outer-diameter sample tubes with sample volumes of \(~300\) \(\mu\)L. EPR spectra were simulated with EasySpin 4.0.0 software.\(^{54}\) X-ray photoelectron spectra were obtained using a Kratos Analytical Axis ULTRA spectrometer containing a DLD detector. Solid samples were fixed onto the sample holder with electrical tape. All XPS spectra were referenced to the C 1s peak (284.2 eV). Gaussians were fit under the Co 2\(p_{3/2}\) and 2\(p_{3/2}\) peaks, where their maxima is reported as the binding energy for the respective peaks. Gel permeation chromatography (GPC) was carried out in THF (flow rate: 1 mL min\(^{-1}\)) at 50°C with a Polymer Labs PL–GPC 50 Plus integrated GPC system with two 300×7.8 mm Jordi gel DVB mixed bed columns, utilising a refractive index detector coupled with a Wyatt Technology miniDAWN™ TREOS® multiple angle light scattering (MALS) detector operating at 658 nm. Literature \(dn/dc\) values of 0.185 and 0.052 for poly(styrene)\(^{55}\), poly(methyl methacrylate)\(^{56}\),
poly(methyl acrylate)\textsuperscript{57} and poly(vinyl acetate) \textsuperscript{55}, respectively, were used. Chemical structures of the monomers and initiators used in this Chapter are shown in Figure 4.3.

![Monomers and initiators used in this Chapter.](image)

**Figure 4.3.** Monomers and initiators used in the studies in this Chapter.

### 4.2.3 X-ray Structure Determination

Single crystal X-ray crystallographic analysis of \(\text{Co(Sal)}\textsubscript{NO}_2\cdot\text{THF}\) was performed on a Bruker X8 APEX II diffractometer with graphite monochromated Mo-K\(\alpha\) radiation. A dark red needle crystal of \(C_{28}H_{34}N_4O_6\text{Co}\cdot\text{THF} \ (\text{Co(Sal)}\textsubscript{NO}_2\cdot\text{THF})\), isolated from the slow evaporation of a THF:pentane solution, was mounted on a glass fibre. The data were collected at a temperature of \(-100.0 \pm 0.1^\circ\text{C}\) to a maximum \(2\theta\) value of \(55.0^\circ\). Data were collected in a series of \(\phi\) and \(\omega\) scans in \(0.50^\circ\) oscillations with 10.0-second exposures. The crystal-to-detector distance was 36.00 mm. The structure was solved by direct methods.\textsuperscript{58} The material crystallises with 1 molecule of THF in the asymmetric unit. All non-hydrogen atoms were refined anisotropically. All C-H hydrogen atoms were placed in calculated positions but were not refined. All crystal structure plots were produced using ORTEP-3. A summary of the crystal data and experimental parameters for structure determinations are given in Appendix 1.

### 4.2.4 Calculations

Geometry optimisations were performed using the Gaussian 09 program (Revision A.02)\textsuperscript{59}, the B3LYP functional\textsuperscript{60-61}, and the 6-31G(d) basis set on all atoms. Frequency calculations at the same level of theory confirmed that the optimized
structures were located at a minimum on the potential energy surface. Single point calculations were performed using the same functional and the TZVP basis set of Ahlrichs$^{62-63}$ on all atoms. The corresponding orbital transformation (COT) was used to determine the singularly occupied molecular orbital for each of the Co complexes.$^{64-65}$ AOMix$^{66-68}$ was used for determining atomic orbital compositions employing Mulliken Population Analysis. Bond dissociation energies were calculated using the BP86 functional$^{69}$, and the TZVP basis set following a published procedure.$^{70-72}$

4.2.5 Synthesis

\((N, N'\text{-bis}(3\text{-}\text{tert-Butyl-5-dimethylaminosalicylidene})\text{-trans-1,2-cyclohexanediamine cobalt})\text{(Co(Sal)NMe2)}\):

![N,N'-bis(3-tert-Butyl-5-dimethylaminosalicylidene)-trans-1,2-cyclohexanediamine cobalt](Co(Sal)NMe2)

To a solution of \(H_2(\text{Sal})\text{NMe2}\) (95 mg, 0.18 mmol) dissolved in degassed Et\(_2\)O (3 mL) was added a solution of Co(OAc)\(_2\cdot4\text{H}_2\text{O}\) (45 mg, 0.22 mmol) in degassed MeOH (3 mL). This mixture was stirred under an inert atmosphere overnight, during which time a dark precipitate formed. The solid was collected by filtration and was dried under reduced pressure overnight to afford a dark green precipitate of Co(Sal)$^{NMe2}$. Yield: 43 mg (41%). MS (ESI): m/z (%): 577.3 (100) [Co(Sal)$^{NMe2}$]$^+$. Anal. calcd. (found) for C\(_{32}\)H\(_{46}\)N\(_4\)O\(_2\)Co\(\cdot\)H\(_2\)O: C 64.52 (64.39), H 8.12 (7.84), N 9.41 (9.41).
(N,N'-bis(3-tert-butyl-5-nitrosalicylidene)-trans-1,2-cyclohexanediamine cobalt (Co(Sal)NO2):

To a solution of H2(Sal)NO2 (110 mg, 0.21 mmol) dissolved in degassed Et2O (5 mL) was added a solution of Co(OAc)2•4H2O (50 mg, 0.20 mmol) in degassed MeOH (5 mL). This mixture was stirred under an inert atmosphere for 15 minutes, in which time an orange precipitate formed. The solid was collected by filtration and was washed with MeOH, then dried under reduced pressure overnight. The resulting orange solid was recrystallized from THF/pentane (1:1) to afford long dark red crystals of Co(Sal)NO2•THF. Yield: 63 mg (46%). MS (ESI): m/z (%): 582.2 (100) [Co(Sal)NO2]+. Anal. calcd. (found) for C28H34N4O6Co•THF: C 58.80 (58.77), H 6.48 (6.61), N 8.57 (8.65).

4.3 Results and Discussion

4.3.1 Synthesis

The cobalt complexes Co(Sal)R were synthesized in good yields from the metallation of the corresponding ligands H2(Sal)R with Co(OAc)2•4H2O under an inert atmosphere (Scheme 4.3). Co(Sal)NO2 yielded crystals suitable for X-ray analysis, using THF/pentane as the recrystallization solvents. The molecular structure of Co(Sal)NO2•THF is shown in Figure 4.4 and selected crystallographic data for the complex are presented in Appendix 1. Co(Sal)NO2•THF exhibits an essentially square planar geometry at the Co center with a molecule of THF weakly coordinated in the axial position (Co-O_{THF} ~ 2.21 Å). The dihedral angle between the N-Co-O planes is 9°, likely due to the steric interaction between the two ortho tert-butyl groups.
Scheme 4.3. Synthesis of Co(Sal)$^R$.

Figure 4.4. POV-ray representation of Co(Sal)$^{NO2}$•THF. Thermal ellipsoids at 50% probability, hydrogen atoms excluded. Selected interatomic distances (Å) and angles (°): Co(1)-O(4), 1.901; Co(1)-O(3), 1.895; Co(1)-N(5), 1.876; Co(1)-N(2), 1.874; N(5)-C(7), 1.292; N(2)-C(6), 1.288; O(4)-C(15), 1.296; O(3)-C(13), 1.291; Co(1)-O(100), 2.211; O(3)-Co(1)-O(4), 86.9(4); O(4)-Co(1)-N(5), 93.5(7); O(3)-Co(1)-N(2), 93.4(8); N(2)-Co(1)-N(5), 852(7).

4.3.2 Electrochemistry

Redox processes for Co(Sal)$^R$ were probed by cyclic voltammetry (CV) in CH$_2$Cl$_2$ using tetra-$n$-butylammonium perchlorate ($^n$Bu$_4$NClO$_4$) as the supporting electrolyte. Three quasi-reversible, one-electron redox processes were observed for R = tBu, OMe and NMe$_2$, where only a single redox process was observed for R = NO$_2$ due to the limitations of the solvent window (Figure 4.5). The reversibility of these processes were evaluated via comparison of the peak-to-peak difference ($E_{pa}$ – $E_{pc}$) for a specific redox process to that of the Fc$^{II}$/Fc couple under identical conditions (Table 4.1). The three redox couples can be assigned to the metal center (Co$^{II}$/Co$^{III}$) and the two redox-active...
The redox chemistry of the tBu, and OMe derivatives have been reported previously with the first redox process assigned as a metal centered one-electron (Co$^{II}$/Co$^{III}$) couple, depending on the choice of counterion and the use of donating solvents.\textsuperscript{50,73} The positive shift in redox potential for the NO$_2$ derivative is due to the presence of electron withdrawing groups in the \textit{para} position. The positive shift in the potential for the NO$_2$ derivative results in only one of the redox processes being visible by CV within the limits of the solvent window. It should be noted that the electrochemistry experiment for Co(Sal)$^{\text{NO}_2}$ was performed with precipitate obtained directly from its metallation reaction, as the crystalline Co(Sal)$^{\text{NO}_2}\cdot$THF was not soluble in CH$_2$Cl$_2$. Overall there is a clear shift in the redox potentials towards more negative (lower) values as the electron donating ability of the \textit{para}-substituents is increased (NMe$_2$ > OMe > tBu > NO$_2$), which was observed for their Ni analogues (See Chapters 2 and 3).

### Table 4.1. Redox Potentials for Co(Sal)$^{R}$ versus Fc$^+/Fc^a$.\textsuperscript{53}

<table>
<thead>
<tr>
<th>Complex</th>
<th>$E_{1/2}$(V)</th>
<th>$E_{1/2}$(V)</th>
<th>$E_{1/2}$(V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(Sal)$^{\text{NO}_2}$</td>
<td>0.30 (0.15)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Co(Sal)$^{\text{tBu}}$</td>
<td>0.06 (0.17)</td>
<td>0.73 (0.13)</td>
<td>0.950 (0.20)</td>
</tr>
<tr>
<td>Co(Sal)$^{\text{OMe}}$</td>
<td>0.00 (0.16)</td>
<td>0.44 (0.15)</td>
<td>0.780 (0.18)</td>
</tr>
<tr>
<td>Co(Sal)$^{\text{NMe}_2}$</td>
<td>-0.28 (0.16)</td>
<td>-0.11 (0.14)</td>
<td>0.220 (0.14)</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Peak-to-peak differences in brackets (|$E_{pa} – E_{pc}$| in V). Peak-to-peak difference for the Fc$^+/Fc$ couple at 298 K is ca. 0.12 V.
Figure 4.5. Cyclic voltammograms of Co(Sal)$^R$: (a) R = NO$_2$; (b) R = tBu; (c): R = OMe; (d): R = NMe$_2$ in CH$_2$Cl$_2$ at 298 K.
Conditions: 1 mM complex, 0.1 M $^n$Bu$_4$NClO$_4$, scan rate 100 mV s$^{-1}$.

4.3.3 X-ray Photoelectron Spectroscopy

The electronic structures of Co(Sal)$^R$ were investigated by XPS (Figure 4.6). Referenced to the C 1s binding energy, the Co 2p$_{3/2}$ and Co 2p$_{1/2}$ binding energies of all
four $\text{Co(Sal)}^R$ complexes indicate a common $+II$ oxidation state for Co (Table 4.2).\textsuperscript{74-76}

The binding energy is the energy required to eject an electron from a particular orbital (in this case, the Co 2p orbital) to the continuum. A lower binding energy indicates the electron populates an orbital of higher energy, while a higher binding energy suggests the opposite. Comparing the binding energies a general trend is observed: as the electron donating ability of the \textit{para}-ring substituents increases, the Co 2p\textsubscript{3/2} and 2p\textsubscript{1/2} binding energies decrease. This is in line with the electrochemical properties of these complexes, where the oxidation potential decreases with more electron rich complexes. These data are further evidence for the influence of the \textit{para}-ring substituents on the electron density at the metal center.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure46}
\caption{X-ray photoelectron spectroscopy (XPS) spectra of $\text{Co(Sal)}^R$, specifically showing the Co 2p\textsubscript{3/2} and 2p\textsubscript{1/2} binding energies (Red: $R = \text{NO}_2$; Black: $R = \text{tBu}$; Blue: $R = \text{OMe}$; Green: $R = \text{NMe}_2$).}
\end{figure}
<table>
<thead>
<tr>
<th>Complex</th>
<th>Binding Energies (eV)ᵃ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Co (2p₃/2)</td>
</tr>
<tr>
<td>Co(Sal)NO₂</td>
<td>798</td>
</tr>
<tr>
<td>Co(Sal)tBu</td>
<td>797</td>
</tr>
<tr>
<td>Co(Sal)OMe</td>
<td>796</td>
</tr>
<tr>
<td>Co(Sal)NMe₂</td>
<td>796</td>
</tr>
</tbody>
</table>

ᵃ Referenced to C 1s (284.2 eV)

4.3.4 Continuous Wave Electron Paramagnetic Resonance

The X-band EPR spectra of the complexes Co(Sal)ⁿ were studied at 20 K and are consistent with a low spin d⁷ Coⁿ⁺ (S = 1/2) ground state (Figure 4.7).⁷⁷-⁷⁸ Based on previous work of Daul and co-workers, and the fitting of the experimental EPR data, Co(Sal)tBu, Co(Sal)OMe and Co(Sal)NMe₂ all exhibit a |yz, 2A₂⟩ ground state in frozen PhMe (Table 4.3). This result is consistent with other reported four-coordinate Coⁿ⁺-salen complexes.⁷⁷-⁷⁸ Co(Sal)NO₂•THF was not soluble in PhMe, thus it was dissolved in a 2:1 mixture of PhMe:THF and subsequently frozen for EPR analysis. While the EPR spectrum of Co(Sal)tBu, Co(Sal)OMe and Co(Sal)NMe₂ were identical within experimental error, the spectrum of Co(Sal)NO₂ displays a different pattern, suggesting a different ground state for this complex (Figure 4.7). EPR fitting analysis provides evidence for a |z², 2A₁⟩ ground state for Co(Sal)NO₂ under these conditions, consistent with a five-coordinate structure (likely THF adduct).⁷⁹ It should be noted that hyperfine coupling constants used to simulate the spectra of the complexes are approximate due to large unresolved hyperfine coupling arising from the interaction of the radical with neighboring spin active nuclei such as nitrogen.⁷⁷-⁷⁸ This analysis is further corroborated by theoretical calculations (See Section 4.3.5).
Figure 4.7. X-band EPR spectra of 1 mM frozen solutions of $\text{Co(Sal)}^R$ at 20 K. Red: $\text{Co(Sal)}^{\text{NO}_2}\text{THF}$ (in 2:1 PhMe:THF); Black: $R = \text{tBu}$; Blue: $R = \text{OMe}$; Green: $R = \text{NMe}_2$. Grey spectra are respective simulations. Conditions: Frequency: 9.384 GHz for $\text{Co(Sal)}^{\text{NO}_2}$, 9.383 GHz for $\text{Co(Sal)}^{\text{Bu}}$, 9.383 GHz for $\text{Co(Sal)}^{\text{OMe}}$ and 9.385 GHz for $\text{Co(Sal)}^{\text{NMe}_2}$; Power = 2.0 mW; modulation frequency = 100 kHz; modulation amplitude = 0.4 mT.
Table 4.3. X-band EPR simulation parameters for Co(Sal)R.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$g_x$</th>
<th>$g_y$</th>
<th>$g_z$</th>
<th>$A_x$ (MHz)</th>
<th>$A_y$ (MHz)</th>
<th>$A_z$ (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(Sal)NO$_2$</td>
<td>2.56</td>
<td>2.30</td>
<td>2.00</td>
<td>410</td>
<td>196</td>
<td>346</td>
</tr>
<tr>
<td>Co(Sal)Bu</td>
<td>3.21</td>
<td>1.88</td>
<td>1.98</td>
<td>400</td>
<td>80</td>
<td>125</td>
</tr>
<tr>
<td>Co(Sal)OMe</td>
<td>3.21</td>
<td>1.89</td>
<td>1.99</td>
<td>400</td>
<td>80</td>
<td>125</td>
</tr>
<tr>
<td>Co(Sal)NNMe$_2$</td>
<td>3.19</td>
<td>1.89</td>
<td>1.99</td>
<td>400</td>
<td>80</td>
<td>125</td>
</tr>
</tbody>
</table>

4.3.5 Theoretical Analysis

Density functional theory (DFT) calculations of the Co(Sal)$^R$ complexes provided further insight into the geometric and electronic structure of these complexes. The optimized geometry for Co(Sal)NO$_2$·THF is in good agreement with the experimental X-ray metrical data (Table 4.4), reproducing the coordination sphere bond lengths to within ±0.02 Å. In the absence of the THF molecule, the predicted coordination sphere bond lengths differ significantly from the experimental data. The calculations of the neutral square planar Co$^{$II$}$ complexes provided further details of the effect of the peripheral substituents on the metal center. Mulliken population analysis predicts the lowest partial charge at Co (0.78) for Co(Sal)NNMe$_2$ and the highest partial charge at Co (0.80) for Co(Sal)NO$_2$ consistent with the expected electronic effects of the para-ring substituents. While this predicted change is small, the correct trend is observed where a higher partial charge was observed for the most electron poor complex, and a low partial charge for the most electron rich complex.

Table 4.4. Experimental and theoretical coordination sphere metrical parameters for Co(Sal)NO$_2$·THF in Å. See Figure 4.4 for atom numbering.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Co-O4</th>
<th>Co-O3</th>
<th>Co-N5</th>
<th>Co-N2</th>
<th>Co-O100</th>
<th>O4-C15</th>
<th>O3-C13</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(Sal)NO$_2$·THF, Experimental</td>
<td>1.901</td>
<td>1.895</td>
<td>1.876</td>
<td>1.874</td>
<td>2.211</td>
<td>1.296</td>
<td>1.291</td>
</tr>
<tr>
<td>Co(Sal)NO$_2$·THF, Calculated</td>
<td>1.901</td>
<td>1.900</td>
<td>1.884</td>
<td>1.893</td>
<td>2.282</td>
<td>1.295</td>
<td>1.293</td>
</tr>
</tbody>
</table>

The electronic structure of the Co(Sal)$^R$ complexes, particularly the nature of the singularly occupied molecular orbital (SOMO) was further examined. Based on the EPR data and fitting, Co(Sal)Bu, Co(Sal)OMe and Co(Sal)NNMe$_2$ all display a common $|yz, 2A_2\rangle$ groundstate. The DFT calculations predict correctly a $d_{yz}$-containing SOMO for these
three derivatives (Figure 4.8). The DFT calculation for the five-coordinate Co(Sal)\textsuperscript{NO2}-THF also predicts correctly a \(d_{z^2}\) SOMO, in line with the \(|z^2, 2A_1\rangle\) ground state based on EPR analysis (Figure 4.7).\textsuperscript{79} Axial ligand binding in this case raises the energy of the \(d_{z^2}\) orbital in comparison to \(d_{yz}\), resulting in the change in electronic ground state.

**Figure 4.8.** Predicted singularly occupied molecular orbital for: a) Co(Sal)\textsuperscript{NMe2}; b) Co(Sal)\textsuperscript{OMe}; c) Co(Sal)\textsuperscript{tBu} and d) Co(Sal)\textsuperscript{NO2}-THF.

The Co-C bond strengths was investigated by theoretical methods as a dormant metal terminated organometallic species is formed in a reversible reaction between the monomer radical and metal complex in RT-OMRP. This equilibrium is heavily dependent on the strength of the metal-carbon bond, which subsequently affects the concentration of radicals in solution for further reaction. Thus the five-coordinate X-Co\textsuperscript{III}(Sal)\textsuperscript{R} complexes (X = 1-phenylethane) were investigated via theoretical methods to better understand the influence of the \(para\)-ring substituents on the axial Co-C bond strength. The Co-C bond dissociation energies (BDE) were calculated by subtracting the energy of the X-Co\textsuperscript{III}(Sal)\textsuperscript{R} reactant from the sum of the energies of the products as shown in Eq. 1.\textsuperscript{70-72} Each species was optimized at the same level of theory and the total energy used to calculate BDE.

\[
X-\text{Co}^{III}(\text{Sal})^R \rightarrow \text{Co}^{II} \text{Sal}^R + X^* \tag{1}
\]

For this series of calculations the BP86 functional was used,\textsuperscript{69} based on prior work by Kozlowski and co-workers on alkyl-Co\textsuperscript{III} macrocycles.\textsuperscript{70-72} The predicted Co-C BDE for Co(Sal)\textsuperscript{NO2} (15.4 kcal/mol) is the highest in the Co(Sal)\textsuperscript{R} series, and is at least
1.3 kcal/mol higher than the values for the $\text{Co(Sal)}^{\text{IBu}}$ (14.1 kcal/mol), $\text{Co(Sal)}^{\text{OMe}}$ (13.7 kcal/mol) and $\text{Co(Sal)}^{\text{NMe2}}$ (13.3 kcal/mol) derivatives. The trend in predicted Co-C BDE is consistent with the relative strength of electron donation from the para-substituents, resulting in an increased Lewis acidity at the metal center. The predicted BDE values are lower than those previously reported for alkyl cobalt salen complexes (methyl, ethyl, etc.), likely due to the increased steric bulk of 1-phenylethane and presence of an additional axial ligand in the previous work.\textsuperscript{82} Overall, as the electron donating ability of the para-substituents is increased in the series, the calculated Co-C BDE decreases. This suggests that the more electron rich complex should be the most active in RT-OMRP, which is indeed observed (See Section 4.3.6).

### 4.3.6 Organometallic Mediated Radical Polymerization

Although recent research has significantly expanded the number of active catalytic systems in OMRP\textsuperscript{15,17-18}, ligand design still plays an important role in increasing both the monomer scope and efficacy of OMRP catalysts. While the effect of carbon-halogen bond strengths on atom transfer radical polymerization (ATRP) has been studied both experimentally and computationally, no similar data have been compiled for OMRP systems. Few investigations of systematic variation of ligand substituents have been reported, but a better understanding of the role of the metal-carbon bond strengths will facilitate improved control of polymerizations. To better understand the impact of bond strength, the $\text{Co(Sal)}^R$ complexes were investigated for reversible termination OMRP. The electronic variation from para-ring substituent modification is anticipated to significantly alter the Co-C bond strengths, allowing for the tuning of this system to facilitate reactivity towards different monomers. This complements recently reported degenerative transfer OMRP of vinyl acetate by a $\text{Co(Sal)}^{\text{IBu}}$ complex.\textsuperscript{45}

Variation of the para-substituent in $\text{Co(Sal)}^R$ complexes had an interesting effect on the behavior of the complexes in the RT-OMRP of styrene (Table 4.5). As the electron donating ability of the substituents increased, conversion increased (from 55% in 1 hour for $\text{Co(Sal)}^{\text{NO2}}$ to 85% in 1 hour for $\text{Co(Sal)}^{\text{NMe2}}$). The decreased electron density around the metal center of $\text{Co(Sal)}^{\text{NO2}}$ can be attributed to this trend, as it would increase the stability of the dormant species and decrease propagating radical
concentrations. This is in line with theoretical results, where Mulliken population analysis of the Co(Sal)R derivatives shows decreasing partial charge at Co for more electron donating para-ring substituents (See section 4.3.5). Co(Sal)NO₂ is predicted to have the most Lewis acidic metal center of the series, resulting in the highest Co³⁺-carbon BDE. Theoretical molecular weights of the polymer, Mₙ,th, were calculated using Eq. 2 by taking into account the relative concentrations of the monomer and initiator, molecular weight of the monomer and the percent conversion determined by GPC. The observed Mₙ values, determined by GPC, were in reasonable agreement with the theoretical values for less electron rich complexes Co(Sal)NO₂ and Co(Sal)²Bu, but much greater deviations between theoretical and experimental values were observed for Co(Sal)³Me and Co(Sal)⁴Me₂. This suggests that electron rich complexes impart less control over the concentration of radical terminated chains, in line with their predicted decrease in BDE.

\[ M_{n,th} = \left[ [M]_0/2[I]_0 \times MW_{monomer} \times \text{conversion} \right] + MW(\text{catalyst}) \]  

(2)

In all cases, the PDIs were broad (1.65-2.38), indicating that these polymerizations were not well-controlled and suggesting that irreversible termination reactions were prevalent. While reversible formation of Co-C bonds controlled the polymerization under these conditions, classic metrics of controlled polymerization were not observed, unlike the recently reported DT-OMRP of vinyl acetate using Co(Sal)²Bu.45 The steric bulk of the ortho-tBu groups and the increased reaction temperature (120°C) relative to DT-OMRP conditions (60°C) may contribute to limiting RT-OMRP control.

**Table 4.5. Styrene polymerization data for Co(Sal)R at 120°C.**

<table>
<thead>
<tr>
<th>Complex</th>
<th>Conversion (%)</th>
<th>Mₙ,th</th>
<th>Mₙ</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(Sal)NO₂</td>
<td>55</td>
<td>5340</td>
<td>4630</td>
<td>2.23</td>
</tr>
<tr>
<td>Co(Sal)²Bu</td>
<td>61</td>
<td>5880</td>
<td>5800</td>
<td>1.78</td>
</tr>
<tr>
<td>Co(Sal)³Me</td>
<td>72</td>
<td>6770</td>
<td>14310</td>
<td>2.38</td>
</tr>
<tr>
<td>Co(Sal)⁴Me₂</td>
<td>85</td>
<td>7920</td>
<td>9110</td>
<td>1.65</td>
</tr>
</tbody>
</table>

Bulk styrene polymerization, 1 hour at 120°C, initiated with AIBN, with complex : initiator : monomer ratio of 1:0.6:100.
To study whether the high polymerization temperature of 120°C leads to undesired side reactions and broadened polydispersities, the polymerization of styrene using V-70 as the initiator at 65°C was examined (Table 4.6). As expected, less conversion occurred at lower temperatures, as the formation of the dormant species is favored and the concentration of radical terminated propagating chains are reduced. Unexpectedly, PDIs were broader, with more deviation between theoretical and experimental molecular weights indicating that the lower temperatures were not preventing side termination reactions. The productive, if uncontrolled, polymerization at this lower temperature is also suggestive that the monomer scope of DT-OMRP by $\text{Co(Sal)}^{\text{Bu}}$ may be limited to monomers that form stronger cobalt-carbon bonds at these temperatures.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Conversion (%)</th>
<th>$M_n,\text{th}$</th>
<th>$M_n$</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(Sal)$^\text{NO}_2$</td>
<td>33</td>
<td>3440</td>
<td>2450</td>
<td>2.41</td>
</tr>
<tr>
<td>Co(Sal)$^{\text{Bu}}$</td>
<td>32</td>
<td>3380</td>
<td>3760</td>
<td>2.21</td>
</tr>
</tbody>
</table>

Table 4.6. Styrene polymerization data for Co(Sal)$^{\text{Bu}}$ and Co(Sal)$^\text{NO}_2$ at 65°C.

Bulk styrene polymerization, 1 hour at 65°C, initiated with V-70, with complex : initiator : monomer ratio of 1:0.6:100.

Despite reasonable agreement of experimental molecular weights with the theoretical values, the broad PDIs of 1.6-2.4 indicated that styrene polymerization was inadequately controlled by Co complexes $\text{Co(Sal)}^R$. To further investigate this, the kinetic data for the polymerization of styrene by $\text{Co(Sal)}^{\text{Bu}}$ was examined. Although the plot of $\ln([M]_0/[M]_t)$ was linear for the first 2 hours with $k_{\text{obs}} = 0.40 \text{ h}^{-1}$, deviations after this time indicated that the radical concentration did not remain constant (Figure 4.9). Interestingly, after just 10 minutes the conversion was 36%, indicating an initial rapid period of polymerization where molecular weights quickly reached ca. 5500 Da. Molecular weights then increased in a linear fashion for the first hour, up to ca. 7200 Da at 56%. However, after this point the molecular weights stagnated, remaining around 7000 Da for the rest of the polymerization (Figure 4.9).
This behavior suggests catalytic chain transfer (CCT, Scheme 4.4), resulting in olefin-terminated polymeric chains, which was confirmed by the presence of olefin end-groups at δ 6.2 ppm in the 1H NMR spectra of the polymer samples (Figure 4.10). Many CoII complexes are excellent CCT catalysts, particularly the cobaloximes and cobalt porphyrins83-84, and it is likely that low metal-carbon bond dissociation energies of the dormant species results in high radical concentrations which, coupled with a high concentration of CoII, favors β-hydrogen abstraction. Re-initiation from the metal-hydride species gives new propagating chains, resulting in the broad PDIs which increase from 1.62 at early stages of the polymerization to 2.04 at 80% conversion. Importantly, by altering the monomer concentration the maximum molecular weight of the resulting olefin-terminated polymer chains can be tuned. For instance, with 500 equivalents of monomer the molecular weights are increased to ca. 20,000 Da, achieved from 25% conversion onwards (Figure 4.11). These moderate-length, olefin-terminated poly(styrene) chains could potentially be used as building blocks for extended macromolecular structures and offer an alternative to the short-chain oligomers traditionally synthesised through efficient CCT polymerizations. Attempted controlled radical polymerizations mediated by molybdenum85-86 and iron87-89 catalysts have previously been reported to yield olefin-terminated poly(styrene) through CCT processes, with the molecular weights of the polymers obtained typically ca. 1000-5000 Da.
Scheme 4.4. Catalytic chain transfer (CCT) mechanism.

Figure 4.10. $^1$H NMR spectrum of polystyrene, showing olefin end-groups at $\delta = 6.1$-$6.2$ ppm and adjacent methane groups at $\delta = 3.1$ ppm.
Figure 4.11. Plots of a) \(\ln([M_i]/[M_f])\) vs. time and b) molecular weight vs. conversion for bulk styrene polymerization at 120°C using Co(Sal)\(^{18}\text{Bu}\) and AIBN.

Conditions: Monomer : catalyst : initiator ratio of 500:1:0.6 used.

The polymerization of the more reactive methyl methacrylate monomer using Co(Sal)\(^{18}\text{Bu}\) proceeded rapidly (70 % conversion in 15 minutes) and yielded molecular weights which were significantly lower than the theoretical values, with surprisingly narrow PDIs (ca. 1.24). Examination of crude samples revealed multimodal GPC traces, with the loss of much of the low molecular weight fraction due to precipitation during work up resulting in much narrower polydispersity traces in the product samples (Figure 4.12). Catalytic chain transfer was confirmed by the presence of olefin end-groups in the PMMA samples, at \(\delta = 5.47\) and 6.20 ppm (data not shown). The well-established propensity for the methyl methacrylate monomer to undergo catalytic chain transfer reactions\(^{83-84}\) is supported by the formation of this lower molecular weight polymer.

Figure 4.12. GPC traces of crude (red) and worked-up (blue) PMMA samples.
Building from the recently published work on the DT-OMRP of vinyl acetate by a cobalt salen complex \((\text{Co(Sal)}^\text{tBu})\),\(^{45}\) we also examined the four \(\text{Co(Sal)}^R\) complexes for the RT-OMRP of vinyl acetate (Table 4.7). Although a notoriously difficult monomer to control due to the difficulty in activation and control of the equilibrium between the unstabilized radical and the dormant species, vinyl acetate has been successfully polymerized using \(\text{Co(acac)}_2\) and other Co-systems using both V-70 and AIBN initiators.\(^{15-16,18}\) We anticipated that the formation of a stronger metal-carbon bond between the vinyl acetate radical and the Co complex would either hinder CCT and favor controlled radical polymerization or, as expected for a system operating solely by DT-OMRP, form no polymeric products.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Conversion (%)</th>
<th>(M_{n,th})</th>
<th>(M_n)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Co(Sal)}^\text{NO}_2)</td>
<td>17</td>
<td>1850</td>
<td>338300</td>
<td>1.81</td>
</tr>
<tr>
<td>(\text{Co(Sal)}^\text{tBu})</td>
<td>49</td>
<td>4260</td>
<td>1280</td>
<td>1.61</td>
</tr>
<tr>
<td>(\text{Co(Sal)}^\text{OMe})</td>
<td>48</td>
<td>4130</td>
<td>4720</td>
<td>1.29</td>
</tr>
<tr>
<td>(\text{Co(Sal)}^\text{NMe}_2)</td>
<td>50</td>
<td>4310</td>
<td>4240</td>
<td>1.60</td>
</tr>
</tbody>
</table>

Bulk vinyl acetate polymerization, 3 hours at 120°C, initiated with AIBN, with complex : initiator : monomer ratio of 1:0.6:100.

Complex \(\text{Co(Sal)}^\text{NO}_2\) was an unsuccessful mediator of VAc OMRP, with only small amounts of very high molecular weight polymer isolated. The strong electron withdrawing substituent makes the Co center electron poor and irreversible binding of the vinyl acetate monomer to the complex is likely to occur, with a small amount of thermal polymerization yielding the observed high molecular weight polymer. As observed with the styrene system, as more electron donating substituents were incorporated into the \(\text{Co(Sal)}^R\) complexes, monomer conversion increased. However, the substituent effect on polymerization rate was less profound for vinyl acetate, with complexes where \(R = \text{tBu, OMe and NMe}_2\) all yielding ca. 50% conversion in 3 hours. More interesting was the effect on the molecular weight data, with \(\text{Co(Sal)}^\text{tBu}\) yielding molecular weights which were significantly lower than theoretical values. Complexes \(\text{Co(Sal)}^\text{OMe}\) and \(\text{Co(Sal)}^\text{NMe}_2\) both gave poly(vinyl acetate) with molecular weights which were in good agreement with the theoretical values, although the PDI of 1.29 obtained with complex \(\text{Co(Sal)}^\text{OMe}\) suggests that the OMe substituent yields the optimal \(\text{Co(Sal)}^R\)
complex out of this series. However, the reported molecular weight represented only 80% of the sample, with a higher molecular weight peak at ca. 97000 Da making up the other 20% as determined by GPC. This is likely due to an inefficient deactivation process, allowing some chains to propagate in an uncontrolled manner, reducing radical concentration.

4.4 Conclusions

A series of cobalt salen complexes $\text{Co(Sal)}^R$ with varying para-ring substituents were prepared and studied by cyclic voltammetry, X-ray photoelectron spectroscopy, electron paramagnetic resonance spectroscopy and computational methods. Characterization supports the reactive metal center tailored by altering ligand electronics. Electrochemistry showed an inverse correlation between redox potentials and electron donating ability, corroborated by a decrease in the Co $2p_{3/2}$ and $2p_{1/2}$ binding energies measured by XPS. Tuning of the complexes was further evident in the theoretical calculations, where $\text{Co(Sal)}^{\text{NO}_2}$ was predicted to have the highest Co$^{\text{III}}$-carbon bond dissociation energy.

Initial results from RT-OMRP using $\text{Co(Sal)}^R$ illustrate the potential of these complexes in controlled radical polymerization, with the data suggesting that the cobalt-carbon bond strength varies with the ligand substitution. While well-controlled RT-OMRP of styrene under the conditions studied was not observed, DT-OMRP of monomers which are susceptible to $\beta$-hydrogen abstraction, including styrene, was successful at low temperatures. The effects of the para-ring substituents of $\text{Co(Sal)}^R$ on the rate of VAc polymerization with complexes $\text{Co(Sal)}^R$ under DT-OMRP conditions is of considerable interest, and currently under examination. In the future, the RT-OMRP methodology will be used for the synthesis of specific molecular weight, olefin-terminated polymer chains with a wide scope of monomers. For future directions, see Chapter 6.
4.5 References


68. Gorelsky, S. I. AOMix, Program for Molecular Orbital Analysis.


Chapter 5.  Fe$^{III}$ Bipyrrolidine Phenolate Complexes and Their Oxidized Analogue


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LC performed the synthesis, electrochemistry, UV-Vis-NIR, EPR experiments and theoretical calculations. YS collected the rR data. FT helped with the analysis of the EPR data.

5.1 Introduction

Heme proteins, such as cytochrome P450, catalase and peroxidase, have received significant attention in the field of catalysis research due to their remarkable reactivity toward unactivated C-H bonds.$^{1-3}$ The active species, an Fe$^{IV}$-oxo unit coordinated by a porphyrinyl radical cation, is formed through a reaction between the heme system and dioxygen (Scheme 5.1).$^4$ The discovery of this entity has inspired the design and investigation of functional synthetic model systems.
Salen ligands have demonstrated their utility in catalytic applications, partly due to their ability to form stable complexes with many metals in a variety of oxidation states. Importantly, many phenolate containing metallosalen complexes have been shown to exist in the [M(Salen)]⁺ electronic state upon oxidation, demonstrating their utility as redox active ligands. Specifically, Fe salen complexes have been studied as synthetic models of heme systems. Numerous phenolate-containing Fe³⁺ complexes have been investigated, and are capable of undergoing successive oxidations to afford multiple ligand radical species. These Fe complexes employ a variety of amine backbones as starting materials, from macrocyclic to linear amines (Figure 5.1). Chiral diamines, highlighted by Jacobsen’s catalyst, a Mn³⁺-salen complex which employs a trans-1,2-cyclohexanediamine backbone, have also received significant interest due to their ability to induce stereoselectivity during catalysis (Figure 5.1). However, it has also been shown that bis-alkoxy ligands employing the same cyclohexanediamine backbone bind metal ions as a mixture of diastereomers, likely due to ligand flexibility. To this end, a more constrained backbone, such as 2,2'-bipyrrrolidine, has been explored, and has been shown to form metal complexes diastereospecifically. As such, there is increasing interest in developing catalysts incorporating this structural motif (Figure 5.1).
Figure 5.1. Phenolate containing ligands employing macrocyclic, linear, and chiral amine backbones.

Interestingly, reports of ligands with this backbone are limited to symmetric structures, with identical pendant arms. Thus, the synthesis of a dissymmetric ligand represents a unique example, where one redox active phenol and one pyridine moiety are appended to the chiral bipyrrolidine backbone ($\text{HL}^2$, Figure 5.2). The Fe complex of this ligand, along with the symmetric bis-phenolate ligand ($\text{H}_2\text{L}^1$, Figure 5.2), allows for the potential correlation of reactivity with the number of redox active ligand fragments within the complex.
5.2 Experimental

5.2.1 Materials

All chemicals used were of the highest grade available and were further purified whenever necessary. The aminium radical chemical oxidant \([\text{N}(\text{C}_6\text{H}_3\text{Br}_2)_3]^+\text{[SbF}_6]^-\) was synthesized according to published protocols. 3,5-di-tert-butyl-2-hydroxybenzylbromide was prepared from commercially available 2,4-di-tert-butylphenol in two steps by reported procedures. \((S,S)\)-\(H_2L^1\) was prepared by reported methods. The \((R,R)\) complexes were synthesized in an analogous manner starting with \((2R,2'R)-2,2'-\text{bipyrrolidine}\).

5.2.2 Instrumentation

Electronic spectra were obtained on a Cary 5000 spectrophotometer with a custom-designed immersion fiber-optic probe with variable path-length (1 and 10 mm; Hellma, Inc.). Constant temperatures were maintained by a dry ice/acetone bath. Solvent contraction was accounted for in all variable-temperature studies. Cyclic voltammetry (CV) was performed on a PAR-263A potentiometer, equipped with an Ag wire reference electrode, a platinum disk working electrode and a Pt counter electrode.
with $^6$Bu$_4$NClO$_4$ (0.1 M) solutions in CH$_2$Cl$_2$. Decamethylferrocene was used as an internal standard.$^{47}$ Electrolysis was performed by using a PAR-273A potentiostat at 233 K using a large Pt grid as the working electrode. Rotating Disk Electrode (RDE) Voltammetry was performed to monitor electrochemical oxidation using a Radiometer TCV101 speed control unit and an EDI 101 electrode. $^1$H NMR spectra were recorded on a Bruker AV-500 instrument. Mass spectra (positive ion) were obtained on an Agilent 6210 TOF ESI-MS instrument. Elemental analyses (C, H, N) were performed by Mr. Farzad Haftbaradaran and Mr. Paul Mulyk at Simon Fraser University on a Carlo Erba EA1110 CHN elemental analyzer. All EPR spectra were collected using a Bruker EMXplus spectrometer operating with a premiumX X-band microwave bridge and a dual mode resonant cavity (~9.39 GHz in parallel mode, 9.63 GHz in perpendicular mode). Low temperature measurements of frozen solutions used an Oxford Instruments helium temperature-control system and continuous flow cryostats. Samples for X-band measurements were placed in 4 mm outer-diameter sample tubes with sample volumes of approximately 300 µL. Resonance Raman spectra were obtained on a MC-100DC spectrometer (Ritsu Oyo Kogaku) with a Beamlok Kr-ion laser (Spectra-Physics) for 406.7 nm excitation, a holographic supernoch filter (Kaiser Optical Systems), and Symphony CCD detector (HORIBA Jobin Yvon) cooled with liquid N$_2$. Spectra of solvated samples were collected in spinning cells (0.5 cm diameter, 330 rpm) at 223 K at an excitation wavelength $\lambda_{ex} = 406.7$ nm (20 mW), 135° back scattering geometry, and 5 minute data accumulation time. Peak frequencies were calibrated relative to indene standards (accurate to ± 1 cm$^{-1}$).

5.2.3 X-ray Structure Determination

Single crystal X-ray crystallographic analysis of FeL$_1$$^1$Cl and FeL$_2$$^2$Cl$_2$ was performed on a Bruker X8 APEX II diffractometer with graphite monochromated Mo-K$\alpha$ radiation. A dark purple block (FeL$_1$$^1$Cl-MeCN) or dark blue prism (FeL$_2$$^2$Cl$_2$-CH$_2$Cl$_2$) crystal was mounted on a glass fibre. The data were collected at 293 ± 0.1 K to a maximum 2$\theta$ value of 55.0°. Data were collected in a series of $\phi$ and $\omega$ in 0.50° widths with 10.0 second exposures. The crystal-to-detector distance was 50 mm. The structure was solved by direct methods (SIR92)$^{48}$ and refined by least-squares procedures using CRYSTALS (v14.40b)$^{49}$ or ShelXle.$^{50}$ All non-hydrogen atoms were
refined anisotropically. All C-H hydrogen atoms were placed in calculated positions but were not refined. All crystal structure plots were produced using ORTEP-3 and rendered with POV-Ray (v.3.6.2). A summary of the crystal data and experimental parameters for structure determinations are given in Appendix 1.

5.2.4 Oxidation Protocols

Under an inert atmosphere at 195 K, 400 µL of a CH₂Cl₂ solution of the metal complex (4.6 mM) was added to 3.0 mL of CH₂Cl₂. Monitored by UV-Vis-NIR, a saturated solution of [N(C₆H₃Br₂)₃]+[SbF₆]⁻ in CH₂Cl₂ was added in 20 µL additions resulting in clean conversion to the respective one-electron oxidized species.

5.2.5 Calculations

Geometry optimizations were performed using the Gaussian 09 program (Revision D.01), the B3LYP functional, and the 6-31G(d) basis set on all atoms. Frequency calculations at the same level of theory confirmed that the optimized structures were located at a minimum on the potential energy surface. Single point calculations for energetic analysis were performed with the B3LYP functional and the TZVP basis set of Ahlrichs on all atoms. Broken-symmetry (BS) DFT calculations were performed with the same functional and basis set. The corresponding orbital transformation (COT) was used to determine the magnetic orbitals for the oxidized systems. AOMIX was used for determining atomic orbital compositions employing Mulliken population analysis.

5.2.6 Synthesis

(2S,2’S)-[N,N'-bis(1-(3,5-di-tert-Butyl-2-hydroxy-phenylmethyl))-2,2'-bipyrrolidine (H₂L¹):
To a solution of (2S,2'S)-2,2'-bipyrrrolidine (120 mg, 0.86 mmol) in MeCN (5 mL) was added K₂CO₃ (249 mg, 1.80 mmol), followed by a solution of 3,5-di-tert-butyl-2-hydroxybenzylbromide (539 mg, 1.80 mmol) in MeCN (5 mL) dropwise at 0°C. The resultant mixture was warmed and stirred at room temperature for 16 hours and filtered, and the filtrate concentrated in vacuo. The crude product was subject to flash column chromatography using silica gel as the stationary phase (Eluent: 50:1 CH₂Cl₂:MeOH) to afford a colorless oil as ligand H₂L₁. Yield: 634 mg (61%). ¹H NMR (CDCl₃, 500 MHz): δ = 10.62 (br s, 1H, OH), 7.23-7.23 (d, 2H, Ar -H, ²J = 1.9 Hz), 6.83-6.84 (d, 2H, Ar-H, ⁴J = 2.2 Hz), 4.00-4.03 (d, 2H, Ar-H, ²J = 13.5 Hz), 3.39-3.42 (d, 2H, Ar -H, ²J = 13.5 Hz), 3.07-3.10 (m, 2H, Ar-CH), 2.78-2.81 (m, 2H, Ar-CH), 2.19-2.25 (m, 2H, N-CH), 1.99-2.04 (m, 2H, N-CH), 1.74-1.83 (m, 6H), 1.44 (s, 18H, t-Bu), 1.30 (s, 18H, t-Bu). ¹³C NMR (CDCl₃, 100 MHz): δ = 154.2, 140.7, 135.5, 122.9, 122.8, 122.2, 65.6, 59.5, 55.1, 35.0, 34.3, 31.9, 29.7, 25.7, 24.1. MS (ESI): m/z (%): 577.49 (100) [H₂L₁+H]⁺.

(2S,2'S)-[N,N'-bis(1-(3,5-di-tert-Butyl-2-hydroxy-phenylmethyl)])-2,2'-bipyrrrolidine iron (III) Chloride (FeL₁Cl):
To a solution of ligand $\text{H}_2\text{L}^1$ (340 mg, 0.61 mmol) in MeCN (15 mL) was added FeCl$_2$ (77 mg, 0.61 mmol) under aerobic conditions. The solution immediately turned purple upon addition, and was stirred at room temperature for 2 hours, after which it was concentrated in vacuo. The purple powder was recrystallized under an inert atmosphere by slow evaporation of a concentrated solution of FeL$_1$Cl in MeCN to afford dark purple crystals. Yield: 143 mg (36%). MS (HRMS): m/z (%): 666.3599 (100) [M+H]$^+$; Elemental Analysis: calculated (%) for C$_{38}$H$_{58}$N$_2$O$_2$ClFe·MeCN: C 67.88, H 8.69, N 6.10; Found: C 67.82, H 8.83, N 6.24. Solution magnetic moment ($^1$H Evans Method): $\mu_{\text{eff}} = 5.98$.

$(2S,2'S)-[N-(2-(Pyridylmethyl)]-2,2'-bipyrrolidine:

![Image of bipyrrolidine structure]

To a solution of $(2S,2'S)$-2,2'-bipyrrolidine (500 mg, 3.57 mmol) in 1,2-dichloroethane (10 mL) was added K$_2$CO$_3$ (493 mg, 3.57 mmol), followed by 2-pyridinecarboxaldehyde (385 mg, 3.57 mmol). The reaction mixture was stirred at room temperature for 2 hours, then filtered and concentrated in vacuo. The product was dissolved in anhydrous EtOH (30 mL), followed by the addition of 10% Pd/C (150 mg). The reaction mixture was stirred under a H$_2$ atmosphere for 3 days. This mixture was filtered over Celite, and the filtrate was concentrated in vacuo. The crude product was subject to flash column chromatography using neutral alumina as the stationary phase (Eluent: 20:1 CH$_2$Cl$_2$:MeOH) to afford a pale yellow oil as the product. Yield: 645 mg (81%). $^1$H NMR (CDCl$_3$, 500 MHz): $\delta =$ 8.46-8.48 (ddd, 1H, Ar-H, J = 6.2, 2.0, 1.0 Hz), 7.65-7.69 (dt, 1H, Ar-H, J = 9.6, 2.2 Hz), 7.19-7.22 (m, 1H, Ar-H), 7.18 (d, 1H, Ar-H, J = 9.8), 4.11 (d, 1H, Ar-CH, J = 19.7 Hz), 3.85 (d, 1H, Ar-CH, J = 19.7 Hz), 3.49-3.55 (m, 1H, N-CH), 3.40-3.46 (m, 1H, N-CH), 3.11-3.21 (m, 2H, N-CH), 2.93-2.98 (m, 1H, N-CH), 2.63-2.69 (m, 1H, CH), 1.98-2.13 (m, 3H, CH), 1.84-1.94 (m, 3H, CH), 1.53-1.64 (m, 2H, CH). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta =$ 159.3, 148.7, 137.6, 123.0, 122.7, 65.9, 63.4, 61.3, 54.9, 44.5, 28.6, 28.3, 24.5, 24.3. MS (ESI): m/z (%): 232.18 (100) [M+H]$^+$. 

142
(2S,2'S)-[N,N'-1-(2-Hydroxy-3,5-di-tert-butylphenylme-thyl)]-2-(pyridylmethyl)]-2,2'-bipyrrrolidine (HL²):

To a solution of (2S,2'S)-[N-(2-(pyridylmethyl)]-2,2'-bipyrrrolidine (661 mg, 2.86 mmol) in MeCN (15 mL) was added K₂CO₃ (395 mg, 2.86 mmol), followed by a solution 3,5-di-tert-butyl-2-hydroxybenzylbromide (855 mg, 2.86 mmol) in MeCN (20 mL) dropwise at 0°C. The resultant mixture was warmed and stirred at room temperature for 16 hours and filtered, and the filtrate concentrated in vacuo. The crude product was subject to flash column chromatography using silica gel as the stationary phase (Eluent: 20:1 CH₂Cl₂:MeOH) to afford a pale yellow solid as ligand HL². Yield: 855 mg (67%). ¹H NMR (CDCl₃, 500 MHz): δ = 8.52-8.53 (d, 1H, Ar-H, J = 4.3), 7.61-7.64 (dt, 1H, Ar-H, J = 7.6, 0.9), 7.38 (d, 1H, Ar-H, J = 7.7), 7.19 (d, 1H, Ar-H, J = 1.8), 7.13-7.15 (dd, 1H, Ar-H, J = 6.5, 5.5), 6.83 (d, 1H, Ar-H, J = 1.5), 4.22 (d, 1H, Ar-CH, J = 13.4), 4.03 (d, 1H, Ar-CH, J = 14.1), 3.50 (d, 1H, Ar-CH, J = 14.1), 3.39 (d, 1H, Ar-CH, J = 13.5), 3.03-3.07 (m, 1H, N-CH), 2.97-3.00 (m, 1H, N-CH), 2.88-2.91 (m, 1H, N-CH), 2.74-2.78 (m, 1H, N-CH), 2.20-2.29 (m, 2H, N-CH), 1.68-1.98 (m, 8H, CH), 1.40 (s, 9H, t-Bu), 1.27 (s, 9H, t-Bu). MS (ESI): m/z (%): 450.36 (100) [HL²+H]⁺; Elemental Analysis: calculated (found) for C₂₉H₄₃N₃O·0.1 CH₂Cl₂: C 76.29, H 9.50, N 9.17; Found: C 76.57, H 9.51, N 9.25.

(2S,2'S)-[N,N'-1-(3,5-di-tert-Butyl-2-hydroxy-phenylmethyl)]-2-(pyridylmethyl)]-2,2'-bipyrrrolidine iron(III) chloride (FeL²Cl₂):
To a solution of ligand HL² (110 mg, 0.2 mmol) in MeCN (4 mL) was added FeCl₂ (31 mg, 0.2 mmol) under aerobic conditions. The solution immediately turned dark blue upon addition, and was stirred at room temperature for 2 hours, after which it was concentrated in vacuo. The blue powder was recrystallized under an inert atmosphere by the diffusion of diethyl ether into a concentrated solution of FeL²Cl₂ in CH₂Cl₂ to afford dark blue crystals. Yield: 89 mg (63%). MS (HRMS): m/z (%): 574.2041 (100) [FeL²Cl₂+H]+; Elemental Analysis: calculated (%) for C₂₉H₄₂N₃OCl₂Fe•1.2 CH₂Cl₂: C 53.55, H 6.61, N 6.20; Found: C 53.33, H 6.64, N 6.30. Solution magnetic moment (¹H Evans Method): \( \mu_{\text{eff}} = 5.89 \).

5.3 Results and Discussion

5.3.1 Ligand and Complex Synthesis

(S,S)-H₂L¹ was prepared by reported methods, where two equivalents of 3,5-di-
tert-butyl-2-hydroxybenzylbromide was reacted with (2S,2'S)-2,2'-bipyrrrolidine.³⁴⁻³⁵ The synthetic scheme of the dissymmetric ligand (S,S)-HL² is presented in Scheme 5.2. (S,S)-HL² was prepared starting with the condensation of commercially available chiral (2S,2'S)-2,2'-bipyrrrolidine with 2-pyridinecarboxaldehyde, where the formation of the aminal intermediate was confirmed by ¹H NMR, but was not isolated due to its limited stability. This product was immediately subjected to hydrogenation conditions to form (2S,2'S)-[N-(2-(pyridylmethyl))-2,2'-bipyrrrolidine, which was then reacted with one
equivalent of 3,5-di-tert-butyl-2-hydroxybenzylbromide to afford dissymmetric ligand (2S, 2’S)-[N,N’-(1-(3,5-di-tert-butyl-2-hydroxy-phenylmethyl))-2-(pyridylmethyl)]-2,2’-bipyrrrolidine ((S,S)-HL2).

(S,S)-FeL1Cl and (S,S)-FeL2Cl2 were prepared by treating an acetonitrile solution of the corresponding ligand with FeCl2 in air, and the metal complexes were isolated in bulk following the removal of solvents in vacuo. Recrystallization of (S,S)-FeL1Cl (slow evaporation of acetonitrile at -30ºC) and (S,S)-FeL2Cl2 (slow diffusion of diethyl ether into dichloromethane) afforded X-ray suitable crystals in moderate yield. Solution magnetic susceptibility measurements by ¹H Evan’s method revealed that (S,S)-FeL1Cl (µeff = 5.98) and (S,S)-FeL2Cl2 (µeff = 5.89) both contain a high spin, S = 5/2 FeIII center. The (R,R) analogues of these complexes were prepared in a similar manner, starting with (2R,2’R)-2,2’-bipyrrrolidine. For the remainder of the chapter FeL1Cl and FeL2Cl2 refers to the (S,S) complexes.

Scheme 5.2. Synthesis of FeL1Cl and FeL2Cl2.

![Scheme 5.2. Synthesis of FeL1Cl and FeL2Cl2.](image)

Reaction Conditions: (i) 2 equiv. 3,5-di-tert-butyl-2-hydroxybenzylbromide, K2CO3, MeCN; (ii) FeCl2, MeCN; (iii) 2-pyridinecarboxaldehyde, 1,2-dichloroethane, K2CO3; (iv) H2, 10% Pd/C, EtOH; (v) 1 equiv. 3,5-di-tert-butyl-2-hydroxybenzylbromide, K2CO3, MeCN; (vi) FeCl2, O2, MeCN.
5.3.2 X-ray Analysis of FeL₁Cl and FeL₂Cl₂

The molecular structures of FeL₁Cl and FeL₂Cl₂ are presented in Figure 5.3 and Figure 5.4, respectively, and select crystallographic data are shown in Tables 5.1 and 5.2. The solid state structure for FeL₁Cl exhibits a slightly distorted square pyramidal geometry with the expected N₂O₂ coordination sphere from the ligand and an apical chloride ligand, affording an overall neutral complex. The Fe-Namine (Fe1-N1: 2.245 Å, Fe1-N2: 2.131 Å) bond distances are in line with other structurally similar five-coordinate diamine-bisphenolate FeIII complexes.22,30-31 Interestingly, the slight difference in bond distances between the metal ion and the two bipyrrrolidine amine nitrogens have also been observed for other square pyramidal bipyrrrolidine complexes.35,64 This is possibly a result of the sterically demanding ortho tert-butyl moieties, which distort the ligand donors from an ideal square pyramidal geometry. As expected, these bond distances are longer than the Fe-Namine bond distance for Fe(Salen)Cl (2.102, 2.087 Å).65-66 The Fe1-O1 and Fe1-O2 bond distances (1.864, 1.866 Å) are similar to that of Fe-O phenolate in Fe(Salen)Cl (1.882 Å),65-66 while the C1-O1 bond distance is also typical of a phenolate moiety. The donor atoms in FeL₁Cl are forced from the mean equatorial plane by 0.21 to 0.22 Å, and the metal center is positioned 0.54 Å above this plane. These values are greater than those observed in a similar diamine-bisphenolate complex22,31, suggesting a stronger distortion at the metal center. This was reflected in the calculated trigonality index67 \( \tau \) of 0.41, which was defined by the equation \( \tau = (\beta - \alpha)/60 \), where \( \beta \) is the N1-Fe1-O2 angle and \( \alpha \) is the N2-Fe1-O1 angle. Perfectly trigonal bipyramidal and square pyramidal complexes have \( \tau \) values of 1 and 0, respectively. The larger \( \tau \) value observed for FeL₁Cl, in comparison to other 5-coordinate diamine-bisphenolate FeIII complexes with backbone such as ethylenediamine22,31 (\( \tau = 0.31 \)) or homopiperazine30 (\( \tau = 0.20 \)), is likely a result of the more rigid bipyrrrolidine backbone, leading to a more distorted metal center.
Figure 5.3. POV-Ray representation of (S,S)-FeL₁Cl. Thermal ellipsoids at 50% probability, hydrogen atoms excluded. Selected interatomic distances [Å] and angles [°]: Fe(1)-O(1): 1.865, Fe(1)-O(2): 1.866, Fe(1)-N(1): 2.246, Fe(1)-N(2): 2.132, Fe(1)-Cl(1): 2.217, C(1)-O(1): 1.333, C(2)-O(2): 1.317; Angles: N(1)-Fe(1)-O(1): 88.6, N(1)-Fe(1)-N(2): 78.0, N(2)-Fe(1)-O(2): 86.2, O(1)-Fe(1)-O(2): 92.9, N(1)-Fe(1)-O(2): 159.1, N(2)-Fe(1)-O(1): 134.8, N(1)-Fe(1)-Cl(1): 96.1, N(2)-Fe(1)-Cl(1): 109.0, O(1)-Fe(1)-Cl(1): 115.4, O(2)-Fe(1)-Cl(1): 102.1.

Table 5.1. Experimental and calculated coordination sphere metrical parameters for FeL₁Cl and [FeL¹Cl]⁺⁺ in Å.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Fe₁-O₁</th>
<th>Fe₁-O₂</th>
<th>Fe₁-N₁</th>
<th>Fe₁-N₂</th>
<th>Fe₁-Cl₁</th>
<th>C₁-O₁</th>
<th>C₂-O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeL₁Cl, X-ray</td>
<td>1.865</td>
<td>1.866</td>
<td>2.246</td>
<td>2.132</td>
<td>2.217</td>
<td>1.333</td>
<td>1.317</td>
</tr>
<tr>
<td>FeL₁Cl, Calculated</td>
<td>1.857</td>
<td>1.865</td>
<td>2.334</td>
<td>2.225</td>
<td>2.274</td>
<td>1.340</td>
<td>1.335</td>
</tr>
<tr>
<td>[FeL¹Cl]⁺⁺, Calculated</td>
<td>1.824</td>
<td>2.010</td>
<td>2.219</td>
<td>2.227</td>
<td>2.236</td>
<td>1.347</td>
<td>1.278</td>
</tr>
</tbody>
</table>

The solid state structure of FeL²Cl₂ exhibits a slightly distorted octahedral geometry with the expected N₃O coordination sphere of the ligand and two chloride ligands to afford an overall neutral complex (Figure 5.4). The Fe-Namine bond distances are similar to those found for FeL₁Cl, and are significantly longer than the reported Fe-Nimine bond distances for a structurally analogous bisphenolate Fe III salen complex.⁶⁵ The Fe₁-O₁ and C₁-O₁ bond distances are similar to those in FeL₁Cl, supporting the Fe III-phenolate formulation. In addition, tetradentate ligands can bind to a metal center in three possible ways: trans, cis-α, or cis-β (Figure 5.5). The ligand of FeL²Cl₂ occupies a cis-α conformation; it has been shown that labile ligands in this orientation are critical to catalytic activity and stereoselectivity.³⁷-³⁸
Figure 5.4.  POV-Ray representation of (S,S)-FeL²Cl₂.

Figure 5.5.  Possible binding modes of tetradentate ligands in an octahedral geometry.

Table 5.2.  Experimental and calculated coordination sphere metrical parameters for FeL²Cl₂ and [FeL²Cl₂]⁺ in Å.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Fe1-O1</th>
<th>Amine Fe1-N1</th>
<th>Fe1-N2</th>
<th>Fe1-N3</th>
<th>Fe1-Cl1</th>
<th>Fe1-Cl2</th>
<th>Cl1-O1</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeL²Cl₂, X-ray</td>
<td>1.876</td>
<td>2.243</td>
<td>2.253</td>
<td>2.289</td>
<td>2.321</td>
<td>2.314</td>
<td>1.338</td>
</tr>
<tr>
<td>FeL²Cl₂, Calculated</td>
<td>1.859</td>
<td>2.340</td>
<td>2.341</td>
<td>2.335</td>
<td>2.320</td>
<td>2.314</td>
<td>1.332</td>
</tr>
<tr>
<td>[FeL²Cl₂]⁺, Calculated</td>
<td>2.014</td>
<td>2.337</td>
<td>2.289</td>
<td>2.202</td>
<td>2.268</td>
<td>2.259</td>
<td>1.276</td>
</tr>
</tbody>
</table>
The ligand, featuring a (S,S)-bipyrrolidine backbone, coordinates to the metal in a \( \Lambda \) helical manner, as observed for other metal complexes employing this enantiomer as the backbone.\(^{34} \) Conversely, the metal center is coordinated in a \( \Delta \) helical manner when the enantiomer of this ligand was prepared using (R,R)-bipyrrolidine as the backbone (Figure 5.6), demonstrating the induction of chirality from the ligand to metal depending on backbone stereochemistry.\(^{35} \)

![Figure 5.6](image-url)

**Figure 5.6.** POV-Ray representations of (a) (S,S)-FeL\(^2\)Cl\(_2\) (\( \Lambda \) helical geometry) and (b) (R,R)-FeL\(^2\)Cl\(_2\) (\( \Delta \) helical geometry), hydrogen atoms and solvent excluded.

### 5.3.3 Theoretical Analysis of FeL\(^1\)Cl and FeL\(^2\)Cl\(_2\)

DFT calculations were carried out on neutral FeL\(^1\)Cl and FeL\(^2\)Cl\(_2\). In both cases, a high spin \( S = 5/2 \) Fe\(^{III} \) center was predicted to be the lowest in energy, in line with solution state magnetic data. The \( S = 5/2 \) high spin state was favored over the \( S = 3/2 \) intermediate spin state (FeL\(^1\)Cl: +15 kcal/mol; FeL\(^2\)Cl\(_2\): +18 kcal/mol) and the \( S = 1/2 \) low spin state (FeL\(^1\)Cl: +27 kcal/mol; FeL\(^2\)Cl\(_2\): +22 kcal/mol). With the exception of the Fe-N\(_{amine} \) bonds, which can be overestimated by DFT calculations,\(^{68-70} \) optimized structures of FeL\(^1\)Cl and FeL\(^2\)Cl\(_2\) using the B3LYP functional and 6-31G(d) basis set are in good agreement with the solid state data, predicting coordination bond lengths to within \( \pm 0.06 \) \( \text{Å} \) (Tables 5.1 and 5.2). In addition, the slight asymmetry in the
coordination sphere for FeL₁Cl observed in the X-ray structure was also well predicted, where the bulky ortho tert-butyl groups force the two phenolate moieties out of the plane from one another. The trigonality index of this optimized structure is 0.23, further supporting a strongly distorted square pyramidal geometry around the metal center. Of note, a hydrogen bonding interaction was also predicted between the Cl atom and a benzylic proton (Cl⋯H: 2.73 Å), which may further contribute to the predicted asymmetric coordination sphere for FeL₁Cl.

5.3.4 Electrochemistry

Redox processes for FeL₁Cl and FeL²Cl₂, and associated ligands, were probed by cyclic voltammetry (CV) in CH₂Cl₂ by using tetra-n-butyl-ammonium perchlorate ([nBu₄N]ClO₄) as the supporting electrolyte (Figure 5.7). The redox potentials versus ferrocenium/ferrocene (Fc⁺/Fc) are reported in Table 5.3. An irreversible reduction wave was observed for both FeL₁Cl and FeL²Cl₂, corresponding to a metal based reduction from Fe³⁺ to Fe²⁺ in line with previous reports.²⁷,⁷¹ A quasi-reversible one-electron redox process was observed for FeL²Cl₂ at 0.59 V vs. Fc⁺/Fc, which was assigned to a ligand-centered oxidation from phenolate to the corresponding phenoxyl radical species based on comparison to the CV of the ligand HL₂, and is further confirmed by resonance Raman studies (See Section 5.3.6). A second irreversible oxidative process for FeL²Cl₂ was observed at ca. 1.4 V at the limit of the solvent window (Figure 5.8).
Figure 5.7. Cyclic voltammograms of (a) $H_2L^1$ (black) and $FeL^1Cl$ (blue); and (b) $HL^2$ (black) and $FeL^2Cl_2$ (blue) in CH$_2$Cl$_2$ at 233 K. Conditions: 2.5 mM solution, 0.1 M $^9$Bu$_4$NClO$_4$ in CH$_2$Cl$_2$, scan rate 100 mV s$^{-1}$.

For $FeL^1Cl$, two quasi-reversible one-electron oxidation waves were observed, with the first wave assigned to a ligand-centered oxidation similarly to $FeL^2Cl_2$. The Fe$^{III}$ salen complex Fe(Salen)Cl reported by Fujii and co-workers exhibited similar electrochemical behavior, where two one-electron ligand-based oxidative waves were observed at 0.85 V and 0.96 V vs. Fc$^+/Fc$. The $FeL^1Cl$ displays considerably lower oxidation potentials in comparison to Fe(Salen)Cl, likely due to the increased electron donating nature of the amine moieties in comparison to imines. The electrochemical data for Fe(Salen)Cl, and several reports of Fe$^{III}$/Fe$^{IV}$ couples at > 0.9 V vs. Fc$^+/Fc$, suggest that the second oxidative wave of $FeL^1Cl$ is likely a ligand based oxidation. No further oxidation waves were observed for $FeL^1Cl$ when scanning towards more oxidizing potentials (Figure 5.8).
Extended cyclic voltammograms of (a) FeL\textsuperscript{1}Cl\textsuperscript{1}, and (b) FeL\textsuperscript{2}Cl\textsuperscript{2} in CH\textsubscript{2}Cl\textsubscript{2}

Figure 5.8. Extended cyclic voltammograms of (a) FeL\textsuperscript{1}Cl\textsuperscript{1}, and (b) FeL\textsuperscript{2}Cl\textsuperscript{2} in CH\textsubscript{2}Cl\textsubscript{2} at 233 K. Conditions: Asterisks indicates the Fe\textsuperscript{II}/Fe\textsuperscript{III} couple of Cp*Fc. 2.5 mM solution, 0.1 M \textsuperscript{6}Bu\textsubscript{4}NClO\textsubscript{4} in CH\textsubscript{2}Cl\textsubscript{2}, scan rate 100 mV s\textsuperscript{-1}.

The difference between the first and second redox potentials (\(\Delta E_{1/2}\)) can provide insight regarding the amount of electronic coupling between the two redox-active phenolate moieties, as well as the degree of electronic delocalization upon oxidation. Theoretically, in the absence of electronic coupling, a symmetric complex with two redox active moieties should exhibit two redox processes separated by \(\Delta E_{1/2} = \frac{RT}{F} \ln 4\) (i.e. \(\Delta E_{1/2} (233 \text{ K}) = 0.028 \text{ V}\)),\textsuperscript{78} which is often observed as a single, two-electron redox couple due to limited experimental resolution. This was not observed experimentally in this work (Figure 5.7), with two redox processes visible, separated by 0.27 V. The relative stability towards comproportionation of the monooxidized species (\(K_c\)) can be described by Equations 1 to 3 using \(\Delta E_{1/2}\).
\[ [\text{ML}] + [\text{ML}]^{**} \leftrightarrow 2[\text{ML}]^* \]  

(1)

\[ K_c = \frac{[\text{ML}^*]^2}{[\text{ML}][\text{ML}^{**}]} \]  

(2)

\[ K_c = \exp \left( \frac{\Delta E_{1/2}^F}{RT} \right) \]  

(3)

**Table 5.3.** Redox Potentials for Fe complexes versus Fc⁺/Fc.

| Complex   | \( E_{\text{red}} \) (V) | \( E_{1/2}^+ \) (V) | \( E_{1/2}^- \) (V) | \( \Delta E_{1/2} \) (V) | \( K_c \)  
<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>FeL¹Cl</td>
<td>-1.16</td>
<td>0.59 (0.10)</td>
<td>0.86 (0.13)</td>
<td>0.27</td>
<td>6.9 x 10⁵</td>
</tr>
<tr>
<td>Fe(Salen)Cl¹⁸</td>
<td>-</td>
<td>0.85</td>
<td>0.96</td>
<td>0.11</td>
<td>2.4 x 10²</td>
</tr>
<tr>
<td>FeL²Cl₂</td>
<td>-1.01</td>
<td>0.59 (0.10)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Peak-to-peak differences in brackets (|\( E_{pA} - E_{pc} \)| in V). Peak-to-peak difference for the Fc⁺/Fc couple at 233 K is ca. 0.13 V.

The values of \( K_c \) and \( \Delta E_{1/2} \) for FeL¹Cl, reported in Table 5.3, suggest moderate coupling between the two redox-active phenolates. This pattern has also been observed for the Cu complex of H₂L¹, which exhibits a \( \Delta E_{1/2} \) of 0.14 V and a \( K_c \) of 1.1 x 10³. In comparison, the Ni²-salen complex [Ni(Sal)⁴Bu]⁺⁺, which is a case where strong coupling between the two redox-active phenolates occurs, exhibits a \( \Delta E_{1/2} \) of 0.48 V and a \( K_c \) of 2.6 x 10¹⁰ (See Chapter 2). Furthermore, Fujii and co-workers hypothesized that the increased charge of the metal center (M III vs. M II) leads to a contraction of the metal d orbital manifold, which limits delocalization of the ligand radical due limited orbital overlap. This is also in good agreement with our experimental results.

### 5.3.5 Electronic Spectroscopy

The electronic absorption spectra of FeL¹Cl and FeL²Cl₂ are typical of high spin Fe III phenolate complexes (Figure 5.9). A characteristic phenolate to Fe III charge transfer band is observed in the visible region (FeL¹Cl: 17600 cm⁻¹ (3500 M⁻¹ cm⁻¹); FeL²Cl₂: 15500 cm⁻¹ (3800 M⁻¹ cm⁻¹)). The broad feature at higher energies is
tentatively assigned to an amine to Fe$^{III}$ charge transfer band.$^{26-27}$ Chemical oxidation using aliquots of the aminium radical oxidant $[\text{N(C}_6\text{H}_3\text{Br}_2)_3]^{+}\text{[SbF}_6]^{-}$ ($E_{\text{ox}} = 1.1$ V vs. Fe$^+/\text{Fc}$ in CH$_2$Cl$_2$) under an inert atmosphere at 195 K resulted in new spectra with isosbestic points ($\text{FeL}_1\text{Cl}$: 20600 and 15300 cm$^{-1}$; $\text{FeL}_2\text{Cl}_2$: 12400 cm$^{-1}$), suggesting clean conversion of the neutral to the oxidized species. Substantial changes were observed upon oxidation, most notably the appearance of a new and intense band in the visible region ($[\text{FeL}_1\text{Cl}]^{\text{+*}}$: 25500 cm$^{-1}$ (9000 M$^{-1}$ cm$^{-1}$); $[\text{FeL}_2\text{Cl}_2]^{\text{+*}}$: 24100 cm$^{-1}$ (8300 M$^{-1}$ cm$^{-1}$)), which was assigned to a $\pi-\pi^*$ transition of a phenoxyl radical species as previously observed for other phenoxyl radical-containing compounds.$^{27}$ In addition, a bathochromic shift and decrease in the intensity of the phenolate to Fe$^{III}$ CT band was also observed ($\text{FeL}_1\text{Cl}$: 17600 cm$^{-1}$ (3500 M$^{-1}$ cm$^{-1}$); $[\text{FeL}_1\text{Cl}]^{\text{+*}}$: 16700 cm$^{-1}$ (2800 M$^{-1}$ cm$^{-1}$); $\text{FeL}_2\text{Cl}_2$: 15500 cm$^{-1}$ (3800 M$^{-1}$ cm$^{-1}$); $[\text{FeL}_2\text{Cl}_2]^{\text{+*}}$: 14400 cm$^{-1}$ (2100 M$^{-1}$ cm$^{-1}$)). A similar pattern of these bands has been observed for an analogous Fe$^{III}$ phenoxyl radical complex.$^{27}$ Half-lives at room temperature ($[\text{FeL}_1\text{Cl}]^{\text{+*}}$: $t_{1/2} = \text{ca.} 6$ hours; $[\text{FeL}_2\text{Cl}_2]^{\text{+*}}$: $t_{1/2} = \text{ca.} 12$ minutes) precluded isolation of the oxidized species in the solid state for X-ray analysis.

Figure 5.9. UV-Vis-NIR spectra of (a) $\text{FeL}_1\text{Cl}$ (black), $[\text{FeL}_1\text{Cl}]^{\text{+*}}$ (red), and (b) $\text{FeL}_2\text{Cl}_2$ (black) and $[\text{FeL}_2\text{Cl}_2]^{\text{+*}}$ (red) in CH$_2$Cl$_2$ at 195 K. Intermediate gray lines measured during the oxidation titration with $[\text{N(C}_6\text{H}_3\text{Br}_2)_3]^{+}\text{[SbF}_6]^{-}$.  

154
Table 5.4. Spectroscopic properties of Fe complexes in CH2Cl2 at 195 K.

<table>
<thead>
<tr>
<th>Complex</th>
<th>λ\text{max}, 10^3 cm^{-1} (ε x 10^3, M^{-1} cm^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeL'Cl</td>
<td>29.3 br (4.4), 17.6 (3.5)</td>
</tr>
<tr>
<td>[FeL'Cl]^+</td>
<td>25.5 (9.0), 18.7 sh (2.9), 16.7 (2.8), 11.1 w (0.52)</td>
</tr>
<tr>
<td>FeL^2Cl_2</td>
<td>25.8 br (3.7), 15.5 br (3.8)</td>
</tr>
<tr>
<td>[FeL^2Cl_2]^+</td>
<td>24.1 (8.3), 21.5 (3.6), 19.2 (3.0), 17.5 (3.1), 14.4 (2.1), 12.6 sh (1.2), 6.9 (1.0)</td>
</tr>
</tbody>
</table>

5.3.6 Resonance Raman Spectroscopy

Resonance Raman spectroscopy (rR) of complexes FeL'Cl and FeL^2Cl_2, and their one-electron oxidized forms [FeL'Cl]^+ and [FeL^2Cl_2]^+, were carried out at the excitation wavelength of 406.7 nm (Figure 5.10). The rR spectra exhibit a new peak upon oxidation: ([FeL'Cl]^+: 1504 cm^{-1}; [FeL^2Cl_2]^+: 1501 cm^{-1}), which was tentatively assigned as the characteristic phenoxyl radical ν_7a band (C-O stretching vibration of a phenoxyl radical). This observation suggests a ligand based oxidation, further confirming the formation of Fe^{III}-phenoxyl radical species for both complexes. A similar series of bands has been observed in the rR spectrum of a related Fe^{III}-phenoxyl radical complex. It should be noted that the phenoxyl radical ν_8a band (C_{ortho}-C_{meta} stretching vibration of a phenoxyl radical), which is expected to be found at ca. 1600 cm^{-1}, could not be detected due to significant fluorescence of the sample (beyond 1600 cm^{-1}).
5.3.7 Continuous Wave X-band Electron Paramagnetic Resonance

The perpendicular mode X-band EPR spectra of FeL\textsuperscript{1}Cl\textsuperscript{2} and FeL\textsuperscript{2}Cl\textsubscript{2}, and their one-electron oxidized forms [FeL\textsuperscript{1}Cl\textsuperscript{2}]+ and [FeL\textsuperscript{2}Cl\textsubscript{2}]\textsuperscript{2+}, were collected at 10 K in CH\textsubscript{2}Cl\textsubscript{2} containing 0.1 M \textsuperscript{6}Bu\textsubscript{4}NClO\textsubscript{4} (Figure 5.11). The EPR spectrum of FeL\textsuperscript{1}Cl displays resonances at g-effective (g\textsubscript{eff}) values of 2, 3.6, 4.3, 4.9 and 9.4. These features are consistent with a high-spin (S = 5/2) Fe\textsuperscript{III} center, where |D| >> h\nu, as commonly observed for such complexes. This spectrum was analyzed using rhombograms, which represents the g\textsubscript{eff} of the three Kramers’ doublets |+1/2>, |+3/2>, |+5/2> as a function of rhombicity E/D. The E/D ratio of 0.20 for FeL\textsuperscript{1}Cl signifies medium-to-strong rhombic distortions, and compares well with a structurally similar complex.\textsuperscript{22} The EPR spectrum of FeL\textsuperscript{2}Cl\textsubscript{2} in CH\textsubscript{2}Cl\textsubscript{2} is markedly different in comparison to FeL\textsuperscript{1}Cl (Figure 5.11). A dominant signal observed at g = 4.3 indicates larger rhombicity, which was reflected in the E/D value of 0.33, and is expected for an octahedral high spin Fe\textsuperscript{III} complex. Electrochemical oxidation of FeL\textsuperscript{1}Cl to [FeL\textsuperscript{1}Cl\textsuperscript{2}]\textsuperscript{2+} induces quenching of the Fe\textsuperscript{III} signal (ca. 90%), likely reflecting antiferromagnetic coupling between the ligand radical and the
Fe$^{III}$ center. In addition, the appearance of a sharp new signal at $g = 2.00$, indicates a minor uncoupled phenoxy radical species.

Figure 5.11. Perpendicular mode X-band EPR spectra of 0.5 mM solutions of: FeL$^1$Cl (left, (a)), electrochemically generated [FeL$^1$Cl]$^{••}$ (left, (b)), FeL$^2$Cl$_2$ (right, (a)), and electrochemically generated [FeL$^2$Cl$_2$]$^{••}$ (right, (b)) in frozen CH$_2$Cl$_2$ with 0.1 M nBu$_4$NClO$_4$ at 10 K.

Due to the presence of the prominent signal at $g = 4.3$ (likely arising from a high spin Fe$^{III}$ contaminant) that superimposes on the spectrum of [FeL$^1$Cl]$^{••}$, X-band EPR analysis in parallel mode was explored. Parallel mode EPR, where the modulating magnetic field is parallel to the applied field, is useful for studying integer electron spin systems, whereas conventional perpendicular mode EPR is better suited for half integer spin systems. Parallel mode EPR have been used in the study of Mn superoxide dismutase$^{83}$ and Photosystem II$^{84-85}$, as well as model Mn$^{III}$, and Fe$^{IV}$($d^4$, $S = 2$) complexes. Indeed, the signals at $g_{eff} = 4.1$ and 2.0 were significantly attenuated, while new broad resonances were observed at ca. 75 mT ($g \approx 9$) and at 150-250 mT (Figure 5.12). The same behavior was observed for [FeL$^2$Cl$_2$]$^{••}$, which also exhibited an intense resonance at 75 mT (Figure 5.12). Such an intense signal at 75 mT has been previously reported for an octahedral Fe$^{III}$ phenoxy radical complex, where the signal was attributed to the $|\Delta M_s| = 2$ transition of a ($S_{total} = 2$) system arising from antiferromagnetic
interactions between the ligand radical and Fe\textsuperscript{III} center.\textsuperscript{28} Thus, both [\textit{FeL}\textsubscript{1}Cl]$^{•+}$ and [\textit{FeL}\textsubscript{2}Cl\textsubscript{2}]$^{•+}$ are assigned as integer spin systems by EPR that arise from antiferromagnetic interactions between the phenoxy radical ($S = 1/2$) and the high spin Fe\textsuperscript{III} ($S = 5/2$) center.

![Figure 5.12. Parallel mode X-band EPR spectrum of a 0.5 mM solution of: (a) electrochemically generated [\textit{FeL}\textsubscript{1}Cl]$^{•+}$ and (b) electrochemically generated [\textit{FeL}\textsubscript{2}Cl\textsubscript{2}]$^{•+}$ in frozen CH\textsubscript{2}Cl\textsubscript{2} with 0.1 M \textit{n}Bu\textsubscript{4}NClO\textsubscript{4} at 10 K.]

5.3.8 Theoretical Analysis of [\textit{FeL}\textsubscript{1}Cl]$^{•+}$ and [\textit{FeL}\textsubscript{2}Cl\textsubscript{2}]$^{•+}$

As their short half-lives precluded isolation of the one-electron oxidized species [\textit{FeL}\textsubscript{1}Cl]$^{•+}$ and [\textit{FeL}\textsubscript{2}Cl\textsubscript{2}]$^{•+}$, DFT calculations were completed to provide valuable insight into their electronic structure. High spin ($S_{\text{total}} = 3$, ligand radical ferromagnetically coupled to the high spin Fe\textsuperscript{III} center) and broken symmetry ($S_{\text{total}} = 2$, ligand radical antiferromagnetically coupled to the high spin Fe\textsuperscript{III} center) solutions were considered. Using the B3LYP\textsuperscript{52-53}/TZVP\textsuperscript{54-55} level of theory, the two spin states were found to be essentially isoenergetic for both complexes, with the broken symmetry solutions being
slightly favored in both cases (0.03 and 0.7 kcal/mol for \([\text{FeL}^1\text{Cl}]^{+}\) and \([\text{FeL}^2\text{Cl}_2]^{+}\), respectively). Using these values, the exchange coupling \(J\) was calculated using the Yamaguchi formula (Equation 4), which is applicable for systems from the strong to weak exchange limit.88-89

\[
J = \frac{E_{HS} - E_{BS}}{\langle S^2 \rangle_{HS} - \langle S^2 \rangle_{BS}}
\]  

(4)

The computed exchange couplings were -2 cm\(^{-1}\) and -48 cm\(^{-1}\) for \([\text{FeL}^1\text{Cl}]^{+}\) and \([\text{FeL}^2\text{Cl}_2]^{+}\), respectively, corresponding to a weak antiferromagnetic \((S_{\text{total}} = 2)\) exchange interaction for these systems. The strength of coupling is reflected in the amount of overlap between a metal based SOMO and a ligand based SOMO, which were found to be 24% and 23% for \([\text{FeL}^2\text{Cl}_2]^{+}\) (Figure 5.13) and \([\text{FeL}^1\text{Cl}]^{+}\) (Figure 5.14), respectively.61-63 For \([\text{FeL}^2\text{Cl}_2]^{+}\), the Fe1-O1 bond distance was predicted to elongate in comparison to the neutral complex (Table 5.2). This is indicative of the formation of a neutral phenoxyl radical upon oxidation, which has decreased electron donating ability relative to the anionic phenolate moiety (\(\text{FeL}^2\text{Cl}_2\): Fe-O 1.859 Å; \([\text{FeL}^2\text{Cl}_2]^{+}\): Fe-O 2.014 Å). Additionally, the C-O bond distances of phenolate/phenoxyl moieties are often indicative of the oxidation state of the ligand due to the formation of a quinoidal ring system upon oxidation. In this case, a shortening of the C-O bond was predicted upon oxidation (\(\text{FeL}^2\text{Cl}_2\): 1.332 Å; \([\text{FeL}^2\text{Cl}_2]^{+}\): 1.276 Å), once again suggesting the formation of a ligand radical species (Table 5.2).
A similar pattern was observed for \( \text{[FeL}^1\text{Cl]}^{\text{2+}} \). Interestingly, the electronic structure was predicted to contain a localized phenoxy radical coupled to the Fe\textsuperscript{III} center, and is highlighted by the predicted changes in C1-O1 (Fe\textsuperscript{L}1\text{Cl}: 1.340 Å; [Fe\textsuperscript{L}1\text{Cl}]\textsuperscript{2+}: 1.347 Å) and C2-O2 bond distances (Fe\textsuperscript{L}1\text{Cl}: 1.335 Å; [Fe\textsuperscript{L}1\text{Cl}]\textsuperscript{2+}: 1.278 Å). In addition, the Fe-O\textsubscript{phenoxy} bond is significantly elongated in comparison to the Fe-
Ophenolate bond (Fe1-O1: 1.824 Å, Fe1-O2: 2.010 Å), which is in line with the Fe-O bond distances of FeL2Cl2 and [FeL2Cl2]+. The shortening of the C2-O2 bond distance signifies phenoxyl radical formation on the ring system containing C2-O2, while the C1-O1 ring remains unchanged. The formation of a localized phenoxyl radical in this symmetric system concurs with the moderate coupling observed in its electrochemistry ($K_c$ value), which has been used previously to evaluate the degree of delocalization for oxidized bisphenolate complexes.12-13,90 This localized ligand radical electronic structure matches the report by Fujii and co-workers, in which the increased metal charge (Mn$^{III}$) leads to d-orbital contraction, limiting delocalization of the ligand radical over the salen ligand scaffold.14

Figure 5.14. Kohn-Sham molecular orbitals for the broken symmetry (S$_{total} = 2$) solution of [FeLCl]$.^+$

Note: AOMix MO breakdown in brackets, see experimental section for details.
5.4 Conclusion

Iron complexes $\text{FeL}^1\text{Cl}$ and $\text{FeL}^2\text{Cl}_2$ were synthesized by reacting FeCl$_2$ with the corresponding symmetric bisphenolate ($\text{H}_2\text{L}^1$) and dissymmetric monophenolate ($\text{HL}^2$) ligands under aerobic conditions. The electrochemistry of $\text{FeL}^1\text{Cl}$ and $\text{FeL}^2\text{Cl}_2$ displayed quasi-reversible redox waves corresponding to the number of redox-active phenolates in the complex. Both complexes were shown to undergo clean one-electron oxidation using a suitable chemical oxidant as measured by UV-Vis-NIR spectroscopy to afford [$\text{FeL}^1\text{Cl}$]$^{+•}$ and [$\text{FeL}^2\text{Cl}_2$]$^{+•}$. The locus of oxidation was demonstrated to be ligand-based by resonance Raman spectroscopy with the presence of the $v_7$ phenoxyl radical band in the oxidized form. This formulation was well supported by EPR spectroscopy and theoretical studies, which further revealed the oxidized species contains a phenoxyl radical antiferromagnetically coupled to the high spin Fe$^{III}$ center. Future work includes chloride ligand replacement (with more labile substituents such as triflate and/or acetonitrile), and its subsequent effect on the catalytic capabilities of the resultant complexes (See Chapter 6).

5.5 References


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Chapter 6. Ongoing and Future Directions

6.1 Thesis Summary

A number of projects involving the design, synthesis, and electronic structure determination of phenolate containing, first-row transition metal complexes were discussed in this thesis. The oxidation potentials of these complexes were predictably decreased upon the increase of substituent electron-donating ability. In general, the electronic structure of a ligand radical depends on the electron-donating ability of the \textit{para}-ring substituent. Complexes with electron-withdrawing (CF$_3$) or weakly electron-donating (tBu) substituents exhibit symmetric electronic structures where the ligand radical is delocalized over both phenolates of the ligand scaffold, while complexes with strongly electron-donating substituents (OMe and NMe$_2$) exhibit asymmetric electronic structures. In addition, the Co complexes with these salen ligands were tested as catalysts in organometallic radical mediated polymerizations. The most electron rich complexes displayed the highest conversion rates, consistent with the predicted bond dissociation energy of the Co$^{III}$-R intermediate. Finally, Fe complexes featuring a chiral bipyrrrolidine backbone, which have been shown to bind metal ions diastereotopically, were also discussed. While reports of ligands including this backbone are predominantly symmetric structures, a novel route to prepare the first example of an asymmetric ligand was successfully established. The two ligands, containing either one or two phenolates, indeed bind to the Fe center diasterotopically.

Through these studies, unique spectroscopic handles for a variety of electronic structures were established using an array of experimental and theoretical techniques. These spectroscopic identifiers represent the foundation for the discovery and characterization of highly reactive ligand radical species that may be invoked during catalysis. Detailed below are some future directions based on results discussed in the previous chapters.
6.2 Chapter 2

The synthesis and characterization of a series of nickel salen complexes and their one-electron oxidized counterparts were discussed in Chapter 2, where the para-substituent on the phenolate moiety varied from strongly electron donating to weakly electron donating (NMe₂ > OMe > tBu). The oxidation potentials of these complexes are in line with the electron donating abilities of the para-substituents, where the locus of oxidation is on the ligand. Symmetric electronic structures were observed for the one-electron oxidized complexes with weakly electron donating substituents ([Ni(Sal)tBu]+•), while an asymmetric electronic structure was observed for those bearing strongly electron donating substituents ([Ni(Sal)OMe]+• and [Ni(Sal)NMe₂]+•), with the lone pair on the para-ring substituents incorporated into the SOMO of the ligand radical. The degree of metal contribution to the SOMO of these oxidized complexes decreases for more electron rich ligands, indicating an energy mismatch between the frontier molecular orbitals of the ligand and metal. The findings in this work represent the groundwork for future studies of metallosalen complexes, as we now have a greater understanding on the role played by the para-ring substituent and their effects on the overall electronic structure (i.e. metal vs. ligand-based oxidation, localized vs. delocalized radical character) of the oxidized complexes. Most importantly, spectroscopic signatures unique to localized and delocalized electronic structures of such metallosalen complexes have been identified by both experimental and theoretical means, which can now be applied towards the study of metallosalen complexes in other capacities such as catalysis.

For example, axial ligands, such as pyridine, have been shown to bind to oxidized species [Ni(Sal)]^R+ with a concomitant shift of oxidation locus from the ligand to metal, to yield [Ni^III(Sal)(py)₂]^+. The spectroscopic handle for these species are well known, and one example was discussed in Chapter 3. Furthermore, a recent report has shown that iodosylarenes can bind in a similar axial fashion, specifically to a high valent Mn-salen core, which is capable of C-H activation. Thus, the binding of iodosylarene to [Ni(Sal)]^R+ could yield novel complexes with interesting reactivity (Scheme 6.1). The spectroscopic features of the resultant complex can be compared to those discussed in
Chapters 2 and 3, which will aid in its electronic structure assignment and ultimately correlation with reactivity.

**Scheme 6.1.** Proposed synthesis of $[\text{Ni}^{III}(\text{Sal})^R(\text{PhIO})_2]^+$.  

In addition, the second oxidative wave of these Ni-salen complexes will be explored by using two-electron chemical oxidants (Scheme 6.2).\(^{5,6}\) While the oxidation of $[\text{Ni}^{III}(\text{Sal})^R(\text{py})_2]^+$ results in a Ni$^{III}$-ligand radical species (Scheme 6.2)\(^7\), there has been little study on such multi-electron oxidation in the absence of exogenous donor ligands. Such oxidized species may promote two-electron oxidative chemistry, as observed in Nature by galactose oxidase and the corresponding synthetic model systems.

**Scheme 6.2.** Binding of Axial ligands to $[\text{Ni}^{III}(\text{Sal})^R]^+$ and subsequent oxidation.

### 6.3 Chapter 3

To complement the work in Chapter 2, a salen ligand bearing the electron withdrawing CF$_3$ functionality was investigated and discussed in Chapter 3. The CF$_3$ group was used as an alternative to NO$_2$ (Chapter 4) due to the limited solubility of
Ni(Sal)NO$_2$ in organic solvents such as CH$_2$Cl$_2$. The experimental techniques discussed in Chapter 2, particularly resonance Raman spectroscopy, should be now be used for [Ni(Sal)$_{CF_3}$]$^{2+}$. Furthermore, the binding constant of the axial ligands to [Ni(Sal)$_3$]$^{2+}$, such as pyridine, will be quantified, where the strongest binding is expected for electron deficient complexes. This may serve to explain their activity for reactions such as that presented in Scheme 6.1, and should be consistent with the predicted trend in bond dissociation energy for the Co(Sal)$^R$ complexes discussed in Chapter 4. Finally, the CF$_3$ moiety allows for magnetic investigations of these oxidized species (both [Ni(Sal)$_{CF_3}$]$^{2+}$ and [Cu(Sal)$_{CF_3}$]$^+$) using $^{19}$F NMR, which may provide information on their overall electronic structure.

6.4 Chapter 4

Several ligands described in Chapters 2 and 3 were used to synthesize cobalt complexes, which were discussed in Chapter 4. It was found that the overall oxidation potentials of the cobalt complexes can also be tuned through para-substituent variations. As such, these cobalt complexes have been applied as catalysts in organometallic radical mediated polymerization reactions, where modest catalytic reactivity was found. Interestingly, the para-ring substitutions were found to play a role in catalytic capabilities. As such, it would be prudent to pursue other known reactions that are catalyzed by Co centers, such as the reduction of protons to H$_2$. Preliminary H$_2$ generation studies using these complexes showed modest reactivity mediated by Co(Sal)$^R$ complexes (Figure 6.1). In this case, low valent species are the most catalytically relevant in this reaction, and these species are expected to be more easily accessible for electron deficient complexes. The increase in current response for the reductive wave in the presence of higher concentrations of acid indicates more electrons being passed from the electrode to the acidic solution, signifying reactivity of the low valent species with H$^+$. This was observed for all Co(Sal)$^R$ complexes in the presence of benzoic acid (Figure 6.1). Unfortunately, these complexes were found to be unstable under highly acidic conditions, which was evident by the complete disappearance of the Co$^{II}$/Co$^{III}$ couple in the electrochemistry upon the addition of a stronger acid such as para-toluenesulfonic acid. Such decomposition is likely due to the hydrolysis of the salicylidene moiety.
Therefore, other acids should be investigated: for example, para-cyanoanilinium tetrafluoroborate, which has been previously used for such proton reduction catalysis. Care must be applied to the choice of acid as it even slight changes to the reaction conditions can heavily influence the reactivity observed.

![Figure 6.1.](image)

**Figure 6.1.** Cyclic voltammograms of Co(Sal)$^R$: (a) $R$ = tBu; (b) $R$ = OMe; (c) $R$ = NMe$_2$; (d) $R$ = NO$_2$ versus Fc$^+$/Fc (black spectra) with increasing amounts of benzoic acid added (10 mM increments, grey and red spectra) in THF at 298 K.

Note: Asterisks indicates the Fe$^{II}$/Fe$^{III}$ couple of Cp*Fc. Conditions: 1 mM Co(Sal)$^R$, 1 mM Cp*Fc, 0.1 M Bu$_4$NClO$_4$, scan rate 100 mV s$^{-1}$. 
The aryl nitro moieties, such as those found in $\text{Co(Sal)}^{\text{NO}_2}$, have been found to undergo multi-electron reduction electrochemically to the corresponding aryl hydroxylamine under acidic conditions.$^{15}$ Thus, a Co complex with an electron withdrawing group that is stable towards reduction under acid conditions is of interest. The trifluoromethyl moiety, studied in Chapter 3, fits this criterion, thus the Co complex of the $\text{H}_2\text{Sal}^{\text{CF}_3}$ ligand has been prepared (See Section 6.3.1, Figure 6.2). The electrochemistry and catalytic ability towards $\text{H}_2$ generation of $\text{Co(Sal)}^{\text{CF}_3}$ is under examination.

6.4.1 Synthesis

(N,N'-bis(3-tert-Butyl-5-trifluoromethylsalicylidene))-trans-1,2-cyclohexanediamine

Cobalt (Co(Sal)$^{\text{CF}_3}$):

Under an inert atmosphere, $\text{H}_2\text{Sal}^{\text{CF}_3}$ (100 mg, 0.20 mmol) was dissolved in MeCN (1 mL) and Co(ClO$_4$)$_2$$\cdot$6H$_2$O (65 mg, 0.20 mmol) was added in MeCN (1 mL). NEt$_3$ (50 µL, 0.40 mmol) was added, and the resulting solution was stirred at room temperature overnight. The orange solution was concentrated in vacuo, and the crude material was recrystallized in 1:1 CH$_2$Cl$_2$ : hexanes at -30°C over several days to afford orange crystals. Yield: 60 mg (55%). MS (ESI): m/z (%): 628.19 (100) [Co(Sal)$^{\text{CF}_3}$ + H]$^+$.  

174
Compounds with functional groups in their secondary coordination sphere that can guide protons to the catalytic metal center have been found to produce H₂ at a greatly enhanced rate in an acidic medium.⁸⁻¹²,¹⁶ For example, pendant amine functionalities can be protonated under acidic conditions to form the corresponding ammonium cation. This protonated species reacts rapidly in the proximity of the low valent metal center to generate the hydride species, which can then undergo a similar reaction with another ammonium cation to release H₂. As such, ligand design in next generation of catalysts should include a functional group (such as a carboxylate or an amine) that can facilitate the delivery of protons to the metal center, as well as a reduced salicylidene functionality to increase the stability of the catalyst in an acidic medium (Figure 6.3).
Finally, the methodology discussed in Chapter 4 can be streamlined with the synthetic methodology currently being developed in the Storr lab towards studying bimetallic complexes for catalytic purposes.2

6.5 Chapter 5

The synthesis and characterization of two new Fe complexes featuring the chiral bipyrrrolidine backbone was described in Chapter 5. Preliminary studies using these FeIII-complexes, and comparison to (S,S)-Fe(PDP) (Figure 6.4)17-18, showed limited catalytic activity towards the C-H bond activation of cyclohexane, which has a bond dissociation energy (BDE) of 96 kcal/mol (Scheme 6.2, Table 6.1).19
Figure 6.4. Structure of (S,S)-Fe(PDP). 17-18

Scheme 6.3. Oxidation of cyclohexane by Fe catalysts.

![Diagram of Fe catalysts and reaction scheme]

BDE = 96 kcal/mol

Table 6.1. Preliminary oxidative catalysis of cyclohexane by Fe catalysts.

<table>
<thead>
<tr>
<th>Catalyst used</th>
<th>Cyclohexanol (%)</th>
<th>Cyclohexanone (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(PDP) 17-18</td>
<td>3</td>
<td>32</td>
</tr>
<tr>
<td>FeL1Cl</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>FeL2Cl2</td>
<td>1</td>
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</tr>
</tbody>
</table>


This may be attributed to the high oxidation potentials required to reach an activated species, as well as the stability of the Fe³⁺-complexes in comparison to Fe(PDP). In addition, the lack of reactivity may be due to the high bond dissociation energy of the substrate studied (Table 6.2). Therefore, substrates with lower BDE, such as 1,4-cyclohexadiene (BDE = 77 kcal/mol), dihydroanthracene (BDE = 77 kcal/mol), or triphenylmethane (BDE = 81 kcal/mol) should also be explored. In addition, the combination of metal center oxidation state and the presence of the Cl ligand which occupies a coordination site may also contribute to their limited reactivity. In the future,
replacing the Cl ligand with more labile functionalities as well as the Fe$^{II}$ analogues will be investigated.

**Table 6.2.** C-H Bond Dissociation Energies of potential substrates of interest.$^{19}$

<table>
<thead>
<tr>
<th>Substrates</th>
<th>Name</th>
<th>BDE (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,4-cyclohexadiene</td>
<td>77</td>
<td></td>
</tr>
<tr>
<td>dihydroanthracene</td>
<td>77</td>
<td></td>
</tr>
<tr>
<td>Triphenylmethane</td>
<td>81</td>
<td></td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>96</td>
<td></td>
</tr>
</tbody>
</table>

Ligands with a chiral bipyrrolidine backbone offer a significant advantage over other common backbones by promoting the diastereotopic binding of the metal center, leading to stereochemical induction from the ligand to the metal center. Thus, the catalytic application of these metal complexes towards reactions yielding potential enantiomeric mixtures is of utmost interest. One such reaction stems from a recent report, which makes use of an iron catalyst for the carboxylation of styrene derivatives.$^{20}$ In this report, a planar bis-iminopyridine ligand scaffold was employed, and the formation of a racemic mixture of products was observed. To this end, the synthesis of divalent metal complexes employing HL$^{2}$ (Discussed in Chapter 5) such as Fe$^{II}$, have been achieved (See Section 6.5.1, Figure 6.5). The reactivity of ($R$,$R$)-FeL$^{2}$Cl in C-H bond activation chemistry should be investigated in comparison to its Fe$^{III}$ analogue. In addition, due to difficulties in the isolation of high valent Fe-oxo species for further reactivity studies, two avenues can be further explored. First, the generation of a relatively stable iron nitrido (or imido) from an iron azide complex is of immediate
interest. The corresponding azide complex was synthesized using the parent chloride complex $\text{FeL}_1^1\text{Cl}$ discussed in Chapter 5, and the solid state X-ray structure is shown in Figure 6.6. The photolysis of Fe-azide complexes to generate Fe-nitrido species have been previously reported, and is under investigation.\textsuperscript{21-25}

6.5.1 Synthesis

$(2R,2'R)-[N,N'-(1-(3,5-di-\text{tert}-\text{Butyl}-2-hydroxy-phenylmethyl})-2-(\text{pyridylmethyl})]-2,2'-\text{bipyrrrolidine iron(II)} \text{ chloride } ((R,R)-\text{FeL}_2^2\text{Cl})$:

![Diagram of FeL2Cl](image)

Under an inert atmosphere, to a solution of ligand $(R,R)-\text{HL}_2$ (50 mg, 0.2 mmol) in $\text{Et}_2\text{O}$ (2 mL) was added $\text{FeCl}_2$ (14 mg, 0.2 mmol), followed by $\text{NEt}_3$ (11 $\mu\text{L}$, 0.2 mmol). The solution turns golden brown upon the addition of base, and was stirred at room temperature overnight, during which time an orange precipitate was formed. The reaction mixture was concentrated in vacuo, dissolved in a minimal amount of MeCN, and filtered through Celite. The filtrate was concentrated in vacuo, where it was recrystallized by the diffusion of diethyl ether into a concentrated solution of $\text{FeL}_2^2\text{Cl}$ in $\text{CH}_2\text{Cl}_2$ to afford orange crystals. Yield: 33 mg (55%).
Figure 6.5.  POV-Ray representation of (R,R)-FeL²Cl.

(2R,2'R)-[N,N'-bis(1-(3,5-di-tert-Butyl-2-hydroxy-phenylmethyl))]2,2'-bipyrrrolidine iron (III) azide ((R,R)-FeL¹N₃):

To a solution of FeL¹Cl (50 mg, 0.08 mmol) in a 1:1 mixture of CH₂Cl₂ and MeOH (2 mL) was added a solution of NaN₃ (24 mg, 0.38 mmol) in H₂O (0.2 mL) under aerobic conditions. The solution immediately turned dark red upon addition, and was stirred at room temperature overnight, and then H₂O (4 mL) was added to the reaction mixture. The organic layer was concentrated in vacuo, where the resultant dark red powder was recrystallized by slow evaporation of a concentrated solution of (R,R)-FeL¹N₃ in MeOH to afford dark purple needles. Yield: 41 mg (81%). MS (ESI negative mode): m/z (%): 630.38 (100) [FeL¹]⁺. Elemental Analysis: calculated (%) for C₃₈H₅₈N₅O₂Fe: C 67.84, H 8.69, N 10.41; Found: C 68.26, H 8.69, N 10.53.
Figure 6.6. POV-Ray representation of \((R,R)\)-FeL\(^1\)N\(_3\).

6.6 Other Bipyrrolidine complexes

Another route to explore are Ru analogues of the bipyrrolidine ligands (Scheme 6.3), stemming from a recent report of an isolated Ru\(^{IV}\)-oxo species using a tetradeutentate ligand.\(^{26}\) In addition, a Ru\(^{VI}\)-nitrido species supported by a salen ligand have also been reported\(^{27}\), which was shown to be highly electrophilic in its C-H bond activation of alkanes\(^{28}\), aziridination of alkenes\(^{29}\) and functionalization of alkynes.\(^{30}\) Overall, the study of high valent metal-oxo and nitrido species coordinated to a redox-active ligand is of utmost interest, due to its biological relevance. The reactivity of these new complexes represents exciting prospects for using redox active ligands in catalysis.
Scheme 6.4. Proposed synthesis of Ru analogues.

(S,S)-HL²

6.7 Closing Statement

This thesis outlined the analysis and evaluation of unique spectroscopic handles for a variety of electronic structures through an assortment of experimental and theoretical techniques. These handles will serve as fundamental benchmarks for the discovery and characterization of highly reactive ligand radical species, which will be critical for catalyst design in pursuing ligand radical species for catalysis.

6.8 References


Appendix. X-ray crystal data and experimental parameters for structural determination

<table>
<thead>
<tr>
<th></th>
<th>Co(Sal)$^{NO2}$ • C$_4$H$_8$O</th>
<th>Co(Sal)$^{CF3}$ • 0.5 CH$_2$Cl$_2$ 0.25 C$<em>6$H$</em>{14}$</th>
<th>Cu(Sal)$^{CF3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
<td>C$<em>{30}$H$</em>{34}$F$_6$N$_2$O$_2$Co</td>
<td>C$<em>{32}$H$</em>{36.5}$ClF$_6$N$_2$O$_2$Co</td>
<td>C$<em>{30}$H$</em>{34}$F$_6$N$_2$O$_2$Cu</td>
</tr>
<tr>
<td><strong>Formula Weight</strong></td>
<td>653.64</td>
<td>691.21</td>
<td>632.14</td>
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<td><strong>Space Group</strong></td>
<td>P -1</td>
<td>P-1</td>
<td>P2$_1$/n</td>
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<td><strong>a (Å)</strong></td>
<td>10.9613(3)</td>
<td>9.1984(5)</td>
<td>8.3007(7)</td>
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<tr>
<td><strong>b (Å)</strong></td>
<td>12.0129(3)</td>
<td>13.4773(8)</td>
<td>17.9066(14)</td>
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<tr>
<td><strong>c (Å)</strong></td>
<td>14.1562(3)</td>
<td>14.6858(8)</td>
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<td><strong>α (°)</strong></td>
<td>106.6320(10)</td>
<td>96.277(1)</td>
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<tr>
<td><strong>β (°)</strong></td>
<td>91.9720(10)</td>
<td>101.130(1)</td>
<td>98.9040(15)</td>
</tr>
<tr>
<td><strong>γ (°)</strong></td>
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<td>102.872(1)</td>
<td>90</td>
</tr>
<tr>
<td><strong>V (Å$^3$)</strong></td>
<td>1559.81(7)</td>
<td>1719.23(17)</td>
<td>2934.3(4)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
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<td>2</td>
<td>4</td>
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<tr>
<td><strong>T (K)</strong></td>
<td>293</td>
<td>150</td>
<td>296</td>
</tr>
<tr>
<td>$\rho_{calc}$ (g cm$^{-3}$)</td>
<td>1.392</td>
<td>1.246</td>
<td>1.431</td>
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<td><strong>λ (Å)</strong></td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
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<tr>
<td><strong>μ (cm$^{-1}$)</strong></td>
<td>0.604</td>
<td>0.597</td>
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<td><strong>Reflections with I&gt;2σ(I)</strong> (data)</td>
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<td>5706</td>
<td>5351</td>
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<tr>
<td><strong>wR$_2$ (I&gt;2σ(I))</strong></td>
<td>0.0453</td>
<td>0.2214</td>
<td>0.1626</td>
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<td><strong>R$_1$</strong></td>
<td>0.0467</td>
<td>0.0726</td>
<td>0.440</td>
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<tr>
<td><strong>Goodness-of-fits on F$^2$</strong></td>
<td>1.011</td>
<td>0.907</td>
<td>1.509</td>
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</tbody>
</table>

Table A1. Summary for Co(Sal)$^{NO2}$ and M(Sal)$^{CF3}$ (M = Co, Cu).
<table>
<thead>
<tr>
<th></th>
<th>(R,R)-FeL¹Cl • CH₃CN</th>
<th>(S,S)-FeL¹Cl</th>
<th>(R,R)-FeL²Cl₂ • CH₂Cl₂</th>
<th>(S,S)-FeL²Cl₂ • CH₂Cl₂</th>
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</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C₄₀H₅₆ClIN₃O₂Fe</td>
<td>C₃₈H₅₈ClN₂O₂Fe</td>
<td>C₃₀H₄₄Cl₄N₃OFe</td>
<td>C₃₀H₄₄Cl₄N₃OFe</td>
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<tr>
<td>Formula Weight</td>
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<td>666.16</td>
<td>660.33</td>
<td>660.33</td>
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<td>Space Group</td>
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<td>H₃</td>
<td>P2₁2₁2₁</td>
<td>P2₁2₁2₁</td>
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<td>a (Å)</td>
<td>12.2668(2)</td>
<td>27.55(2)</td>
<td>14.399(2)</td>
<td>9.0064(9)</td>
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<tr>
<td>b (Å)</td>
<td>12.9694(2)</td>
<td>27.55(2)</td>
<td>24.101(4)</td>
<td>14.6395(15)</td>
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<tr>
<td>c (Å)</td>
<td>25.5151(4)</td>
<td>12.754(11)</td>
<td>26.777(4)</td>
<td>24.409(2)</td>
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<tr>
<td>α (°)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
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<tr>
<td>β (°)</td>
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<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>γ (°)</td>
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<td>120</td>
<td>90</td>
<td>90</td>
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<tr>
<td>V (Å³)</td>
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<td>8382(16)</td>
<td>9292(2)</td>
<td>3218.3(6)</td>
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<td>9</td>
<td>12</td>
<td>4</td>
</tr>
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<td>T (K)</td>
<td>293</td>
<td>296</td>
<td>90.0(1)</td>
<td>296</td>
</tr>
<tr>
<td>ρ&lt;sub&gt;calc&lt;/sub&gt; (g cm⁻³)</td>
<td>1.157</td>
<td>1.188</td>
<td>1.416</td>
<td>1.363</td>
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<td>λ (Å)</td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td>μ (cm⁻¹)</td>
<td>0.472</td>
<td>0.510</td>
<td>0.861</td>
<td>0.828</td>
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<td>Reflections with I&gt;2σ(I) (data)</td>
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<td>6734</td>
<td>15133</td>
<td>5228</td>
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<tr>
<td>wR₂(I&gt;2σ(I))</td>
<td>0.0421</td>
<td>0.1084</td>
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<td>R₁</td>
<td>0.0427</td>
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<td>Goodness-of-fits on F²</td>
<td>1.938</td>
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<td>1.011</td>
<td>1.055</td>
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Table A3. Summary for (R,R)-FeL1N3 and (R,R)-FeL2Cl.

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<th>(R,R)-FeL1N3</th>
<th>(R,R)-FeL2Cl</th>
</tr>
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<tr>
<td>Formula</td>
<td>C_{38}H_{58}N_{5}O_{2}Fe</td>
<td>C_{30}H_{44}Cl_{3}N_{3}OFe</td>
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<td>Formula Weight</td>
<td>672.74</td>
<td>624.88</td>
</tr>
<tr>
<td>Space Group</td>
<td>P2\text{1}2\text{1}</td>
<td>P2\text{1}2\text{1}</td>
</tr>
<tr>
<td>a (Å)</td>
<td>9.6176(5)</td>
<td>7.8881(4)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>14.9269(9)</td>
<td>17.7854(9)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>25.3918(14)</td>
<td>22.4016(11)</td>
</tr>
<tr>
<td>α (°)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β (°)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>γ (°)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>3645.3(4)</td>
<td>3142.8(3)</td>
</tr>
<tr>
<td>Z</td>
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<td>4</td>
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<tr>
<td>T (K)</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>(\rho_{\text{calc}}) (g cm(^{-3}))</td>
<td>1.226</td>
<td>1.321</td>
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<td>(\lambda) (Å)</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td>(\mu) (cm(^{-1}))</td>
<td>0.453</td>
<td>0.762</td>
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<td>Reflections with (I&gt;2\sigma(I)) (data)</td>
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<td>6293</td>
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<td>wR(_2) ((I&gt;2\sigma(I)))</td>
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<td>R(_1)</td>
<td>0.0241</td>
<td>0.0322</td>
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<td>Goodness-of-fits on (F^2)</td>
<td>1.030</td>
<td>1.047</td>
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</table>