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Adventures in Transition Metal and Actinide Chemistry:
Multidentate N-Heterocyclic Ligands for the Study
of *d*- and *f*-Element Bonding and Reactivity

By

Ashleigh Lauren Ward

A dissertation submitted in partial satisfaction of the
requirements for the degree of
Doctor of Philosophy
in
Chemistry
in the
Graduate Division
of the
University of California, Berkeley

Committee in charge:

Professor John Arnold, Chair
Professor T. Don Tilley
Professor Jeffrey A. Reimer

Spring 2014

Adventures in Transition Metal and Actinide Chemistry:
Multidentate N-Heterocyclic Ligands for the Study
of *d*- and *f*-Element Bonding and Reactivity

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Ashleigh Lauren Ward

**Adventures in Transition Metal and Actinide Chemistry:
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of *d*- and *f*-Element Bonding and Reactivity**

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Doctor of Philosophy in Chemistry
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Professor John Arnold, Chair

Chapter 1:

A series of actinide–transition metal heterobimetallics have been prepared, featuring thorium, uranium and cobalt. Complexes incorporating the binucleating ligand $N[o-(NHCH_2P^iPr_2)C_6H_4]_3$ with either Th(IV) (**1.4**) or U(IV) (**1.5**) and a carbonyl bridged $[Co(CO)_4]^-$ unit were synthesized from the corresponding actinide chlorides (Th: **1.2**; U: **1.3**) and $Na[Co(CO)_4]$. Irradiation of the resulting isocarbonyls with ultraviolet light resulted in the formation of new species containing actinide–metal bonds in good yields (Th: **1.6**; U: **1.7**); this photolysis method provides a new approach to a relatively unusual class of complexes. Characterization by single-crystal X-ray diffraction revealed that elimination of the bridging carbonyl and formation of the metal–metal bond is accompanied by coordination of a phosphine arm from the N_4P_3 ligand to the cobalt center. Additionally, actinide–cobalt bonds of 3.0771(5) Å and 3.0319(7) Å for the thorium and uranium complexes, respectively, were observed. The solution-state behavior of the thorium complexes was evaluated using 1H , 1H - 1H COSY, ^{31}P and variable-temperature NMR spectroscopy. IR, UV–vis/NIR, and variable-temperature magnetic susceptibility measurements are also reported.

Chapter 2:

The first examples of actinide complexes incorporating corrole ligands are presented. Thorium(IV) and uranium(IV) macrocycles of $Mes_2(p-OMePh)corrole$ were synthesized via salt metathesis with the corresponding lithium corrole in remarkably high yields (93% and 83% respectively). Characterization by single-crystal X-ray diffraction revealed both complexes to be dimeric, having two metal centers bridged via bis(μ -chlorido) linkages. In each case, the corrole ring showed a large distortion from planarity, with the Th(IV) and U(IV) ions residing unusually far (1.403 Å and 1.330 Å respectively) from the N_4 plane of the ligand. 1H NMR spectroscopy of both the Th and U dimers revealed dynamic solution behavior. In the case of the diamagnetic Th corrole, variable-temperature, DOSY and EXSY 1H NMR spectroscopy was employed, and supported that this behavior was due to an intrinsic pseudorotational mode of the corrole ring about the M–M axis. Additionally, the electronic structure of the actinide corroles

was assessed using UV–visible spectroscopy, cyclic voltammetry and variable-temperature magnetic susceptibility. This novel class of macrocyclic complexes provides a rich platform in an underdeveloped area for the study of non-aqueous actinide bonding and reactivity.

Chapter 3:

A series of divalent first row triflate complexes supported by the ligand tris(2-pyridyl(methyl))amine (TPA) have been investigated as oxygen reduction catalysts for fuel cell applications. $[(\text{TPA})\text{M}^{2+}]^{n+}$ (M= Mn, Fe, Co, Ni and Cu) derivatives were synthesized and characterized by X-ray crystallography, cyclic voltammetry, NMR spectroscopy, magnetic susceptibility, IR spectroscopy and conductance measurements. The stoichiometric and electrochemical O_2 reactivity of the series were examined.

Chapter 4:

Complexes of the ligand tris(2-pyridyl(methyl))amine (TPA) $\{[(\text{TPA})\text{M}^{2+}]^{n+}$ (M= Mn, Fe, Co and Cu) $\}$ presented in chapter 3 were evaluated as electrocatalysts for oxygen reduction. Rotating-ring disk electrode (RRDE) voltammetry was used to examine the catalytic activity of the series of complexes on a carbon support in acidic media, emulating fuel cell performance. The iron complex displayed a selectivity of 89% for four-electron conversion and demonstrated the fastest reaction kinetics, as determined by a kinetic current of 7.6 mA. Additionally the Mn, Co and Cu complexes all showed selective four-electron oxygen reduction ($< 28\% \text{H}_2\text{O}_2$) at onset potentials ($\sim 0.44 \text{ V vs. RHE}$) comparable to state of the art molecular catalysts, while being straightforward to access synthetically and derived from non-precious metals.

Dedicated to my father, Wilbur, whose genuine nature,
loving spirit and good humor will always be with me

Acknowledgments

In the time I have allotted myself to write this section of my thesis, which I assure you is not proportional to its significance, I fear I can never be as eloquent or heartfelt in my language as is deserving to all those who have gotten me to this point. I can only hope that the following pages, conceived in the last minute coffee-filled hours of this marathon, will suffice, and that they somehow convey how indebted and truly grateful I am.

Not everyone has the unique fortune of being bound in both blood and spirit with another as I am with you, Levi. I'm not even sure that fortune is the right word exactly, because so much of what has defined us has been hardship, but I know that we both stand who we are today as a result of all that has passed, and I have to say, I think we're looking pretty damn good. You understand my strengths and weaknesses, my fears and dreams, and all the complex idiosyncrasies that drive me, because we were forged in the same flame (point of information: I may have been watching too much *Game of Thrones* recently...). I deeply cherish this understanding and feel I would not be where I am today were it not for the support it has provided me. I am so proud of you it's crazy, and have been and always will be your biggest fan. I can't wait to see where life takes you and hope you know I am always here for you, unconditionally.

Ever since I can remember, I have had a deep respect and admiration for strong women. Thanks to you, Grandmom, I have grown up being able to carefully and closely observe the qualities of the quintessential strong woman. You've shown me the importance of "life skills" like structure, balance and hard work, but also that good friends and having fun are healthy for the soul. You challenged me to set lofty goals and to accomplish them in a whole hearted manner, but also taught me to take care of myself and to sporadically pause for perspective every now and then. I strive to emulate you in so many ways and will always want nothing more than to make you proud. I can't think of a more fitting self identifier than G-mom, for you truly are a G.

A drastic turning point in the trajectory of my life occurred my junior year in high school with Ms. Russell's (*Mrs.* Russell is her mother!) English class. I honestly don't feel as though anyone had ever truly motivated me until you, Amy. I learned that with perseverance and attention to detail I could not only perform well but stand out. You lured me out of my shell and fostered my self-worth. You taught me the importance of detailed excellence and that I, *Miss* Ashleigh Ward, could achieve it. From the larger things like faith in myself, to the minutia of my grammar Nazi tendencies, everything I learned in your class propelled me forward and continues to serve me exceptionally well to this day. Now I remain *your* obedient servant.

As with Amy's English class, I have no doubt that my journey thus far would be drastically different had I not stumbled into the lives of the Shepherd family. You quite literally took me in off the streets, or the porch as the case may be, as a teenager and blended me in as part of your family. From you, I have learned so much about what it means to be a good mother, father, partner, sister, brother, mentor, friend and advocate. I would never have been able to overcome the many roadblocks (mental, financial and physical) that obstructed my path to success in both high school and college without your support and guidance. I know that we can never be as close as we once were, but you are always in my heart and the lessons I have learned from you all will always be close.

To my friends from home who keep me grounded in reality outside of graduate school: Em, Jessie, Christina, Kyle, Sylvanus, Ben and John. I can't tell you how much it means to just pick

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up where we left off whenever I see you, or to know that the feeling of not fully having your life sorted out quite yet isn't purely a PhD student affliction.

Once getting to graduate school, no one deserves more credit for my safe passage (pun intended) through the first few years of graduate school than you, Casey. From the first year report, to the GRS and qualifying exam, to my first paper, you were my Virgil. You were kind when I was vulnerable, harsh when I needed to shape up, and made me smile when all I wanted to do was cry. I have never had a better mentor and I'm so happy that beyond that I get to call you my friend.

One BAMF by the name of Scott Forsythe Hickey once told me, "Keep away from people who try to belittle your ambitions. Small people always do that but the really great make you feel that you too can become great. When you are seeking to bring big plans to fruition it is important with whom you regularly associate. Hang out with friends who are like-minded and who are also designing purpose-filled lives. Similarly be that kind of a friend for your friends." Okay, fine, that was Mark Twain, but Scott, you passed it along to me as you have countless other words of encouragement over the past five years. Your sense of humor and down-to-earth nature never cease to put a smile on my face, and I can't tell you how fortunate I feel to have found such a kindred spirit in Nerdistan. You have grounded me and given me hope as we've slogged through grad school, but you've also been there as a life coach, and are always available when I need a "Scott's Corner" (watch out Maury!). I am happy beyond words for you and Kate and the life that you will have together. You're the best bro a lady queer could ask for.

Stacy, we've had a rough marriage, but can't you admit there have been good times too? At the very least, I hope you can put on a good face FOR THE CHILDREN, or is that TOO MUCH TO ASK?! As an aside, I'm pretty sure our jokes are funny to no one but us; I love them nonetheless. Thanks for always being around when I needed to complain, or ask for advice, or just be distracted. This is a testament to the quality of our friendship, but also to the fact that, as the most diligent person I've ever met, you are always in lab. I wish you a beautiful spot in the wilderness to call your own, with a golden retriever who will never leave your side. Ben can be on the other side; he's kind of a puppy too.

Despite the noisiness of your beard, your desire to awkwardly hug from the side, and your eagerness to shy away from emotions, Jeff, I'm just going to have to say that I love you; deal with it. You and Anum are truly the best human beings I've ever met through and through. You've seen me at my worst, although I hope at my best too, and still been willing to make dinner, see a movie, get coffee or go to the beach whenever I ask. Thanks for putting up with me and being the most reliable friends I have.

I also want to thank Tiffany, Allie, Erica, Kurt, the Daves, Amy, Billy, Dani, Gaby and Sam for heartfelt conversations, delicious meals, kind gestures, outdoorsy activities and probably too many drinks, as these have gotten me through certain days, weeks and even months of this experience.

As I finish up my time as a PhD student at UC Berkeley, I know that there was no better lab for me to join than the Arnold lab. I tell every new group of students who inquire about joining our group that John somehow manages to be quite hands off, while also being the most available professor I can think of. He isn't going to hover over your shoulder or spoon feed you ideas, but he's always available to brainstorm and troubleshoot. Although the learning curve is steep, the

Acknowledgments

unique independence and skill set gained in the Arnold lab allows you to take ownership of your science and subsequent achievements. This experience grants a particular sense of pride, but also the feeling that you have accrued a knowledge base that reaches far beyond just chemistry and is geared for success moving forward. John, I want to thank you for your mentorship, your kindness and your faith in me.

I want to thank Stefan, Sergio and Pete for helping to get me started in the Arnold lab. A well deserved shout-out also goes to Thomas, Dan and Heather for your support ever since joining our first year, and to the rest of the past and present Arnold group members who have made the 5th floor northwest corner of Latimer a supportive, gregarious, sometimes very odd but never boring, and relentlessly fun place to work. I am grateful to a host of members of the Chang, Long, Raymond, Sarpong and Tilley groups for your advice, help with instrumentation, and countless supplies. To the rest of the Berkeley Chemistry community: from the coffee lab guy, to the woodshop crew, to the ladies of 419, you all make this a uniquely tolerable, dare I say pleasant, place to obtain a PhD. Without the sense of community felt from student to student, lab to lab, and department to department, the science here would not be what it is.

Table of Contents

Chapter 1

Photochemical Route to Actinide–Transition Metal Bonds: Synthesis, Characterization and Reactivity of a Series of Thorium and Uranium Heterobimetallic Complexes.....1

Overview.....	2
Introduction.....	2
Results and Discussion.....	4
Synthesis and Structural Properties.....	4
NMR Spectroscopy.....	13
Infrared Spectroscopy.....	14
Magnetic Susceptibility.....	15
UV–vis/NIR Spectroscopy.....	16
Conclusion.....	18
Experimental Details.....	19
References.....	24

Chapter 2

Synthesis, Solution-Phase Studies and Solid-State Characterization of Thorium(IV) and Uranium(IV) Corrole Complexes.....27

Overview.....	28
Introduction.....	28
Results and Discussion.....	30
Synthesis and Structural Properties.....	30
UV–vis Spectroscopy.....	35
NMR Spectroscopy.....	37
Electrochemistry.....	39
Magnetic Susceptibility.....	42
Conclusion.....	42
Experimental Details.....	43
References.....	46

Chapter 3

Synthesis, Characterization and Dioxygen Reactivity of a Series of First Row Transition Metal Tris(2-pyridylmethyl)amine Complexes.....49

Overview.....	50
Introduction.....	50

Table of Contents

Results and Discussion.....	52
Synthesis and Structural Properties.....	53
Magnetic Susceptibility.....	61
Conductance.....	62
NMR Spectroscopy.....	63
Infrared Spectroscopy.....	64
Dioxygen Reactivity.....	64
Conclusion.....	67
Experimental Details.....	68
References.....	71

Chapter 4

Electrocatalytic Four-Electron Dioxygen Reduction by a Series of Nonprecious Transition Metal Complexes.....74

Overview.....	75
Introduction.....	75
Results and Discussion.....	77
Cyclic Voltammetry.....	77
Cyclic Voltammetry in O ₂ Saturated Solution.....	82
Thin-Film Cyclic Voltammetry.....	86
Thin-Film Cyclic Voltammetry in O ₂ Saturated Solution.....	88
Rotating Ring-Disk Voltammetry.....	89
Rotating Disk Voltammetry.....	90
Conclusion.....	91
Experimental Details.....	92
References.....	93

Future Directions

Overview.....	97
Actinide Corrole Complexes.....	97
Synthesis.....	97
Characterization.....	99
Theory.....	99
Actinide N ₄ P ₃ Complexes.....	99
Synthesis.....	99
Characterization.....	102
Theory.....	103

Chapter 1

Photochemical Route to Actinide–Transition Metal Bonds: Synthesis, Characterization and Reactivity of a Series of Thorium and Uranium Heterobimetallic Complexes

Overview

The study of metal–metal bonding is a robust field of great importance to bioinorganic chemistry, catalysis and materials science. On a more fundamental level, understanding the nature of metal–metal interactions furthers our knowledge of chemical structure and bonding. Actinide metal–metal bonds however are under-explored as compared to the *s*, *p* and *d* block. The following chapter describes the synthesis and characterization of a series of actinide–transition metal heterobimetallics supported by the binucleating ligand N[*o*-(NHCH₂PⁱPr₂)C₆H₄]₃. Actinide–transition metal bonds were achieved via a novel photolytic approach, which resulted in the first thorium–cobalt bond and a rare uranium–cobalt bond. Portions of this chapter have previously been published in: Ward, A. L., Lukens, W. W., Lu, C. C. and Arnold, J. “Photochemical Route to Actinide–Transition Metal Bonds: Synthesis and Characterization of a Series of Thorium and Uranium Heterobimetallic Complexes.” *J. Am. Chem. Soc.*, **2014**, *136*, 3647.

Introduction

Probing the nature of bonds formed between actinide metals and other elements is important for expanding our understanding of the electronic structure and chemical bonding of the *f*-block elements, and in turn driving its evolution.^{1–6} In the case of metal–metal bonds, those involving the 5*f* elements are fundamentally different from their transition metal and lanthanide counterparts as a result of actinide *f*-orbital participation in bonding, coordinative diversity, and access to a wide range of oxidation states.^{1,7} Understanding these fundamental properties is of importance in nuclear fuel technologies, where small differences in covalency between the 4 and 5*f* elements may provide opportunities to improve fission product separations.^{8–11} Additionally, novel applications utilizing the actinides have recently emerged, including hydrocarbon functionalization, small molecule activation and group atom transfer reactions facilitated by uranium catalysts.¹²

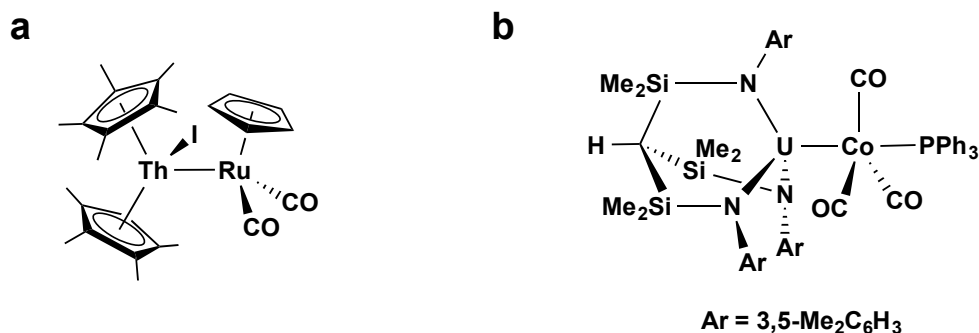


Figure 1.1. Actinide metal–metal bonds. a) The first reported actinide metal–metal bond between thorium and ruthenium. b) The first reported uranium–cobalt bond.

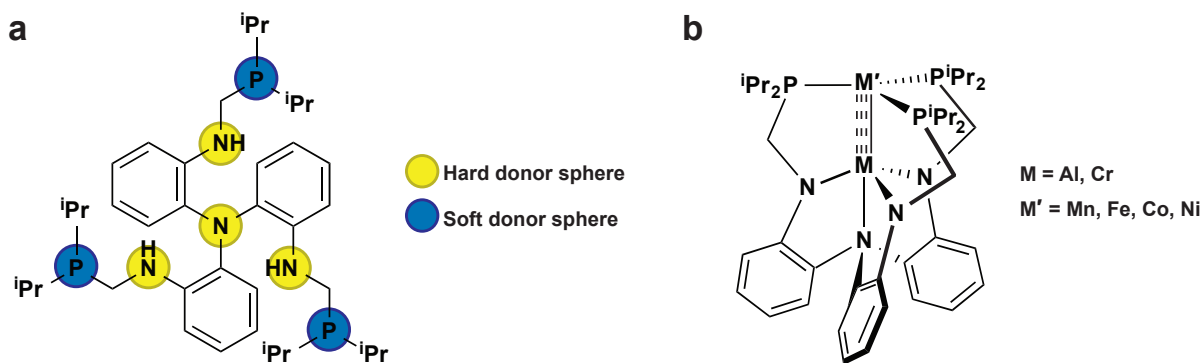


Figure 1.2. a) Ligand of interest $N[\sigma-(\text{NHCH}_2\text{P}(\text{iPr})_2)\text{C}_6\text{H}_4]_3$ (N_4P_3) with hard (yellow) and soft (blue) coordination spheres highlighted. b) Precedented main group and transition metal metal-metal bonded derivatives.

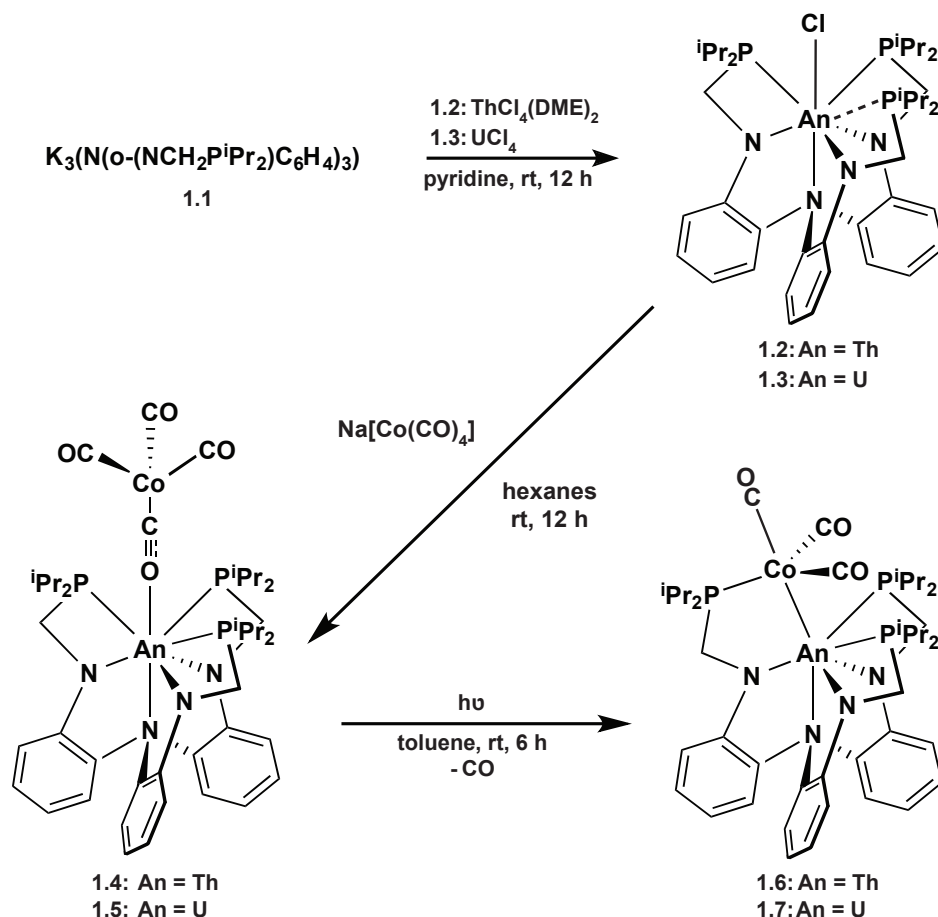
The first actinide-transition metal bond, between Th and Ru, was reported by Marks and co-workers nearly thirty years ago (Figure 1.1a).¹³ In spite of this, f -element metal-metal bonds are still rare in comparison to the multitude of examples for the s , p and d block.¹⁴⁻¹⁶ This is due in part to the fact that while there are a broad range of synthetic routes to metal-metal bonds involving transition metals in particular,¹⁶ the synthesis of actinide analogues has been limited to salt metathesis and elimination reactions. Accordingly, a relatively small number of examples have been reported,¹⁷ establishing uranium bound to iron, ruthenium, rhenium and cobalt (Figure 1.1b), in addition to the first example involving thorium.¹⁸⁻²⁴ Expanding synthetic routes to actinide metal-metal bonds provides an exciting opportunity to develop this field, with the potential to offer new insight into electronic structure and yield alternative modes of bimetallic cooperativity for novel catalytic applications.

The modular nitrogen/phosphorous scaffold, $N[\sigma-(\text{NHCH}_2\text{P}(\text{iPr})_2)\text{C}_6\text{H}_4]_3$ (N_4P_3), has recently been shown to facilitate metal-metal bonding via stabilization through a secondary phosphine coordination sphere, and has thus far been used to couple aluminum and chromium with a series of first row transition metals (Figure 1.2).²⁵⁻²⁷ Here, we show how this hard/soft donor system can be employed to provide a platform for bonding between (hard) actinides and (soft) late transition metals. Two important features of this approach are i) the intermediacy of an isocarbonyl $[\text{Co}(\text{CO})_4]^-$ species that loses CO upon photolysis, and ii) the trapping of the resulting coordinatively unsaturated Co center by a pendent phosphine to yield the metal-metal bonded products. A series of uranium complexes, as well as their diamagnetic thorium analogues, has been synthesized. To the best of our knowledge, this method represents a new route to actinide-transition metal bonds, and results in a rare example of a U-Co bond, as well as the first structurally characterized Th-Co bond. Additionally, these molecules allow for the electronic structure, solution state behavior and magnetic properties of a new series of low-valent actinides to be studied.

Results and Discussion

Synthesis and Structural Properties. The potassium salt of the pro-ligand, $K_3\{N[o-(NCH_2P^iPr_2)C_6H_4]_3\}$ (**1.1**), was prepared by reaction of the triamine with $K[N(TMS)_2]$ in toluene, affording the desired product in quantitative yield. Attempts to use the known lithium analogue were less successful, presumably due to salt incorporation—a common problem in metathesis chemistry with actinide metals.⁷ A uranium starting platform, as well as the diamagnetic thorium analogue, were targeted to allow for a wider range of characterization methods. Accordingly, the complexes $\{N[o-(NCH_2P^iPr_2)C_6H_4]_3\}ThCl$ (**1.2**) and $\{N[o-(NCH_2P^iPr_2)C_6H_4]_3\}UCl$ (**1.3**) were synthesized via combination of **1.1** with $ThCl_4(DME)_2$ ²⁸ and UCl_4 ²⁹ respectively in pyridine (Scheme 1.1). Both reactions were stirred at room

Scheme 1.1. Synthesis of Thorium and Uranium Complexes **1.2–1.7**^a



^aDifferences in phosphine binding in complexes **1.2** and **1.3** are indicated by a dotted line.

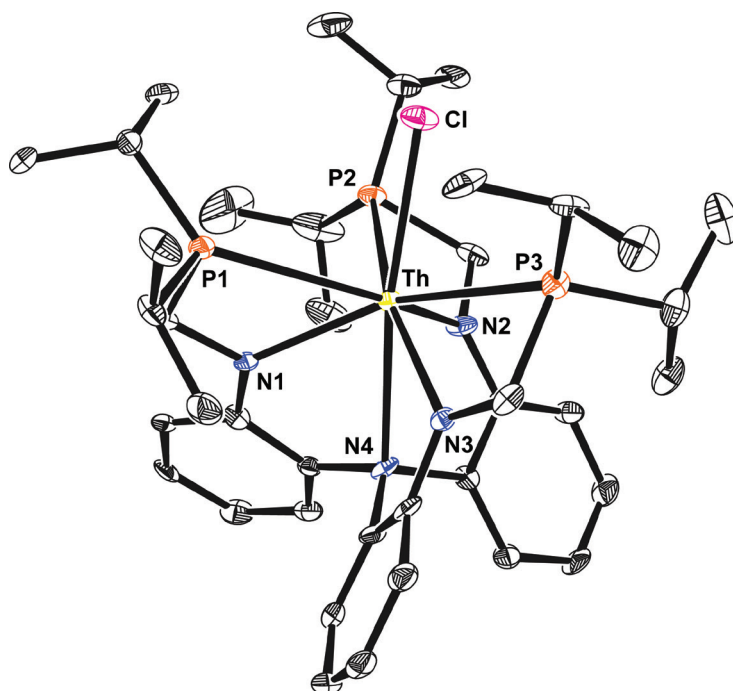


Figure 1.3. Molecular structure of thorium complex **1.2**. Thermal ellipsoids are set to a 50% probability level and hydrogen atoms have been omitted for clarity.

temperature overnight, resulting in a pale yellow solution for the thorium complex **1.2**, and a dark red solution for uranium complex **1.3**. Evaporation of the solvent under vacuum, followed by crystallization from a mixture of diethyl ether (Et_2O) and hexanes at $-40\text{ }^\circ\text{C}$, afforded colorless needles of **1.2** (65% yield) and orange needles of **1.3** (68% yield).

The molecular structure of complex **1.2**, as determined by X-ray diffraction, reveals the coordination about the metal center to be roughly trigonal dodecahedral (Figure 1.3). As with the main group and transition metal N_4P_3 counterparts,²⁵⁻²⁷ phosphine coordination is metal center dependent. The phosphine arms interact with the actinide centers to varying degrees, in addition to the four nitrogen donors of the ligand, consistent with the much larger coordination sphere of the actinides. All three phosphines bind to the thorium center in **1.2**, but only two of the phosphine arms are coordinated in **1.3** (Figure 1.4). This is consistent with the difference in ionic radii ($1.00\text{ }\text{\AA}$ vs. $1.05\text{ }\text{\AA}$ for U(IV) and Th(IV) respectively).³⁰ Despite the small disparity, this variation is often enough to allow for a higher coordination number in the latter.¹ The actinide distortion from the N_3 plane of the ligand is $1.041\text{ }\text{\AA}$ for thorium complex **1.2** and $0.908\text{ }\text{\AA}$ for uranium complex **1.3**. This distortion is far greater than the main group and first row transition metal examples due to the much larger size of the actinide centers. The disparity between the actinide distances themselves is again consistent with differences in radii between them. Complexes **1.2** and **1.3** represent a limited number of actinide complexes that

employ ligands containing both hard and soft donors. Utilizing similar ligand frameworks, highly reactive intermediates have been stabilized for further functionalization with transition metals and lanthanides, meaning **1.2** and **1.3** could provide a unique opportunity to establish orthogonal reactivity patterns using actinides.^{31,32}

As an initial foray into exploring the capability of this platform to facilitate actinide metal–metal bonding, secondary metals known to bind favorably to the phosphine donors were targeted. Treatment of **1.2** or **1.3** with Na[Co(CO)₄] in hexanes at room temperature overnight (Scheme 1.1) resulted in precipitation of the desired products from solution; crystallization from a mixture of toluene and hexanes at -40 °C gave colorless blocks of **1.4** (77% yield) and dark orange blocks of **5** (76% yield). While there is well established literature precedent for carbonyl substitution by phosphines,^{33,34} the oxophilicity of the actinide centers, coupled with the inherent stability of the [Co(CO)₄]⁻ fragment, gave rise to less conventional isocarbonyl compounds **1.4** and **1.5**, as revealed by X-ray diffraction studies (Figures 1.5a and 1.6). Although there are many heterobimetallic transition metal isocarbonyls,^{33,34} there are only five structurally characterized uranium isocarbonyls,^{23,35,36} and we are unaware of any reports for thorium. Uniquely, **1.4** and **1.5** provide heterobimetallic systems suited to photolytic substitution via the carbonyls, while also possessing a secondary coordination sphere capable of stabilizing any resulting unsaturated intermediates.

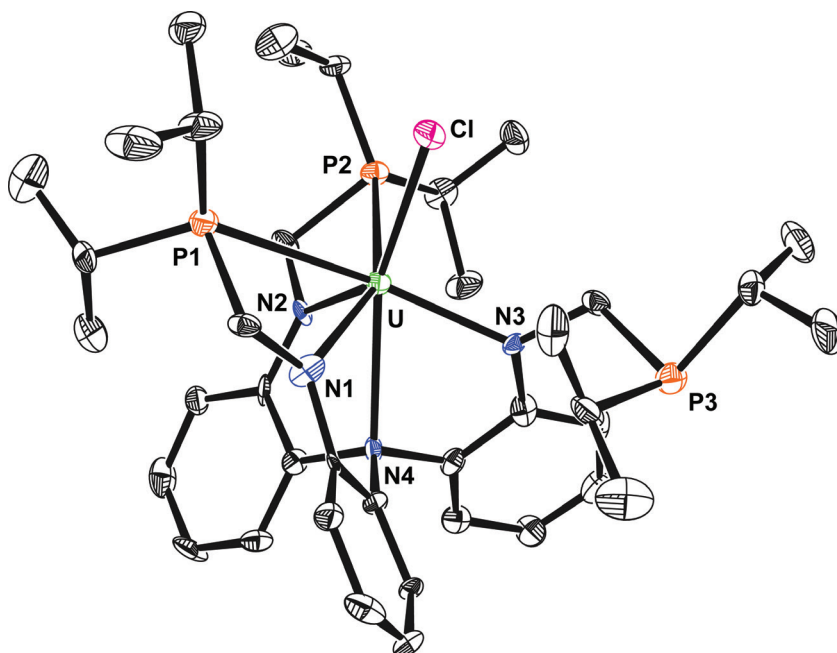


Figure 1.4. Molecular structure of uranium complex **1.3**. Thermal ellipsoids are set to a 50% probability level and hydrogen atoms have been omitted for clarity.

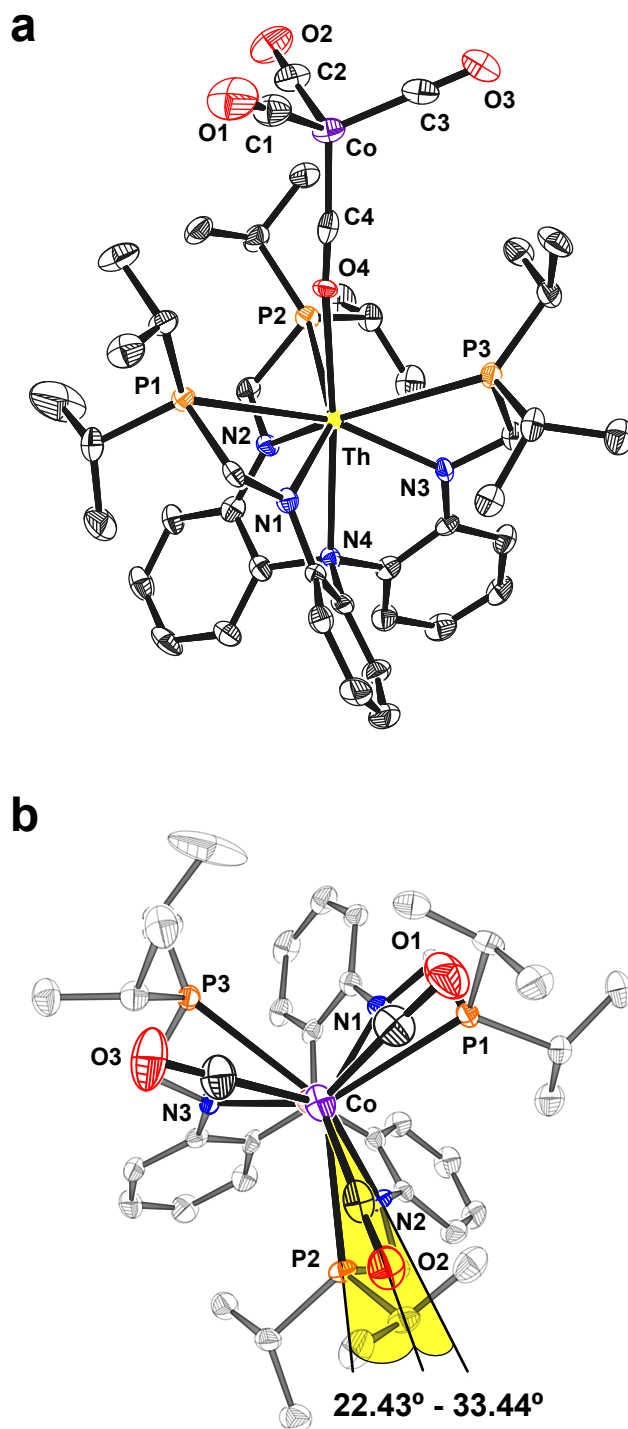


Figure 1.5. a) Molecular structure of thorium complex **1.4**. b) Alternate view of **1.4** along the Co-(μ -CO)-Th axis, illustrating the partially staggered propeller conformation. Thermal ellipsoids are set to a 50% probability level and hydrogen atoms have been omitted for clarity.

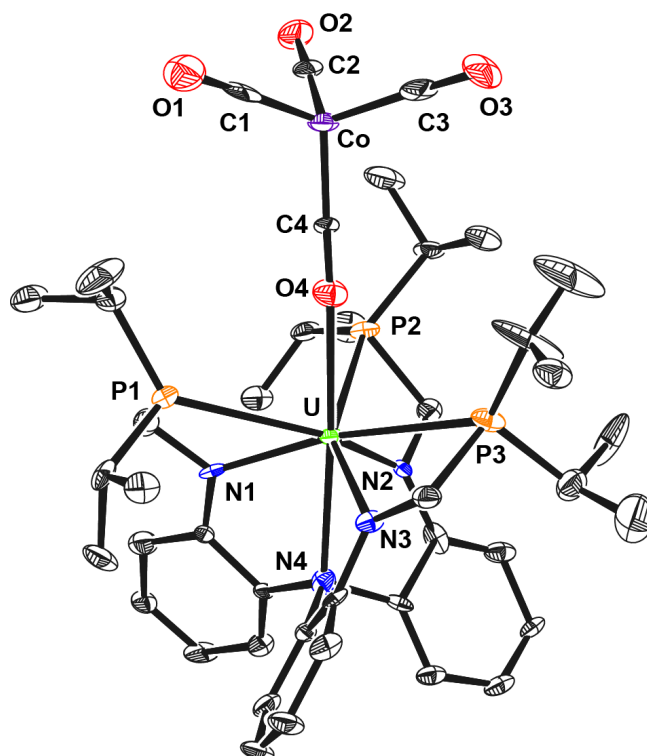


Figure 1.6. Molecular structure of uranium complex **1.5**. Thermal ellipsoids are set to a 50% probability level and hydrogen atoms have been omitted for clarity.

The actinide centers for **1.4** and **1.5** are eight coordinate, with all four nitrogens and the three phosphorus donors bound to the metal centers. Each complex displays a partially staggered conformation in relation to the $\text{Co}(\text{CO})_3$, N_3An and P_3An units respectively (Figure 1.5b). The helical twist along the $\text{An}-(\mu\text{-CO})\text{-Co}$ axis results in torsion angles ranging from 23.43° to 33.44° , presumably to help minimize steric repulsions upon formation of the heterobimetallics.³⁷ The bond lengths and angles observed for **1.4** and **1.5** (Table 1.1) compare well with related uranium isocarbonyls, as well as a Yb compound having an analogous isocarbonyl bridged cobalt unit.³⁸

Chapter 1

Table 1.1. Selected Bond Lengths (Å) and Angles (°) for Complexes **1.2–1.7**

Complex	1.2	1.3 ^a	1.4 ^a	1.5	1.6	1.7 ^a
Bond Lengths (Å)						
M–Cl	2.750(2)	2.672(2)	-	-	-	-
M–N1	2.381(6)	2.270(7)	2.329(3)	2.25(1)	2.318(3)	2.278(5)
M–N2	2.367(5)	2.273(7)	2.336(4)	2.255(9)	2.357(3)	2.291(5)
M–N3	2.339(4)	2.266(7)	2.354(4)	2.25(1)	2.343(3)	2.292(5)
M–N4	2.710(5)	2.616(7)	2.663(4)	2.59(2)	2.602(2)	2.572(4)
M–P1	3.136(2)	3.131(2)	3.225(1)	3.125(3)	3.243(1)	3.125(2)
M–P2	3.212(1)	3.094(2)	3.166(2)	3.178(3)	3.146(1)	3.177(2)
M–P3	3.263(2)	4.737(3)	3.163(1)	3.118(3)	-	-
An–O4	-	-	2.594(4)	2.57(2)	-	-
M–Co	-	-	-	-	3.0771(5)	3.0319(7)
Co–C4	-	-	1.732(6)	1.73(1)	-	-
C4–O4	-	-	1.165(7)	1.15(2)	-	-
C1–O1	-	-	-	-	1.169(6)	1.161(8)
C2–O2	-	-	-	-	1.164(5)	1.158(8)
C3–O3	-	-	-	-	1.150(5)	1.159(7)
Co–C1	-	-	-	-	1.749(5)	1.752(7)
Co–C2	-	-	-	-	1.742(4)	1.750(7)
Co–C3	-	-	-	-	1.773(4)	1.763(6)
Co–P3	-	-	-	-	2.214(1)	2.085(5)
An–C2	-	-	-	-	3.094(4)	3.198(1)
Bond Angles (°)						
N4–An–Co	-	-	-	-	139.32(7)	138.04(9)
Co–C2–O2	-	-	-	-	169.9(4)	170.9(5)
N4–M–X	166.1(1)	154.5(2)	-	-	-	-
An–C4–Co	-	-	174.9(3)	175.8(6)	-	-

^aComplexes **1.3**, **1.4** and **1.7** have more than one molecule in the asymmetric unit and as a result all bond lengths and angles are presented as an average.

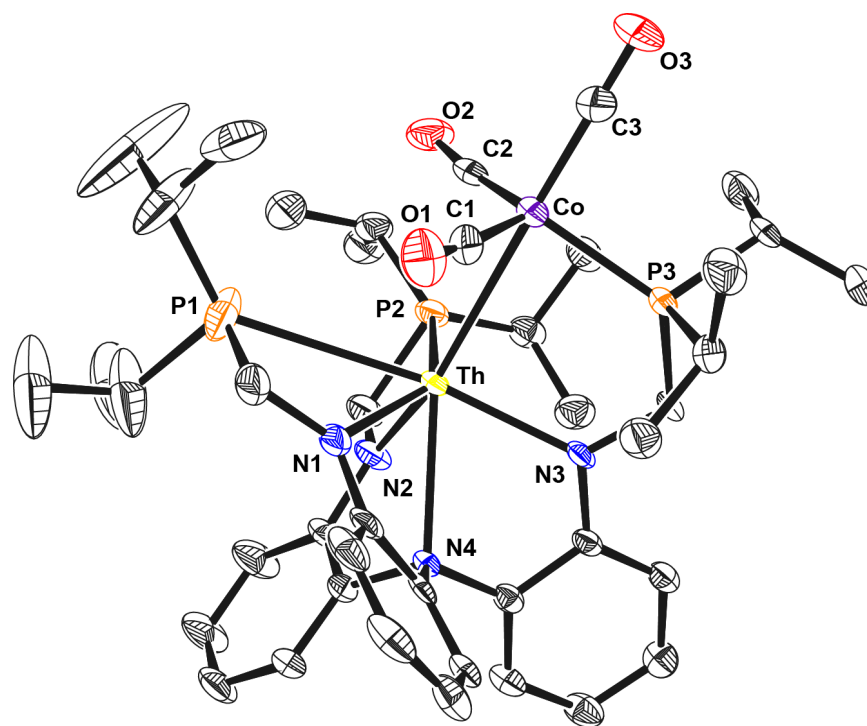


Figure 1.7. Molecular structure of thorium complex **1.6**. Thermal ellipsoids are set to a 50% probability level and hydrogen atoms have been omitted for clarity.

Actinide–transition metal bonds were targeted via UV irradiation of compounds **1.4** and **1.5** as shown in Scheme 1.1. Unlike the bulk of literature concerning photolysis of transition metal carbonyl compounds, which describes either the irradiation of an existing metal–metal bond to promote dissociation, or the facilitation of ligand exchange,^{33,34,39} irradiation of compounds **1.4** and **1.5** results in the formation of an actinide–metal bond (Figures 1.7 and 1.8). Evaporation of the solvent under vacuum, followed by crystallization from a mixture of Et₂O and hexanes at –40 °C, afforded colorless needles of **1.6** (61% yield) and red needles of **1.7** (58% yield).

Formation of metal–metal bonds by this route is unusual for transition metals and, to our knowledge, has not been reported for actinides.^{40–42} Subjecting the isolated compounds **1.4** and **1.5** to subsequent irradiation under the same conditions does not result in further carbonyl ligand substitution. Additionally, **1.6** and **1.7** do not react with CO under either thermal or photochemical conditions to reform **1.4** and **1.5**.

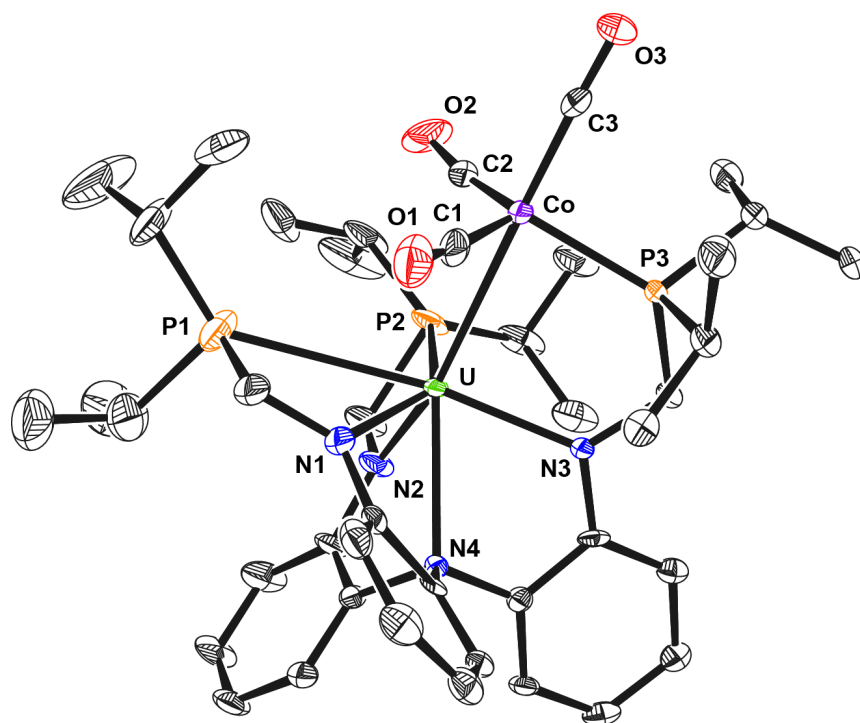


Figure 1.8. Molecular structure of uranium complex **1.7**. Thermal ellipsoids are set to a 50% probability level and hydrogen atoms have been omitted for clarity.

These compounds represent a unique system for comparing the variation in An–M bonding involving two different actinides with identical coordination spheres. The geometry about the metal centers is approximately trigonal bipyramidal, with τ values of 0.88 and 0.85 for the thorium and uranium complexes, respectively.⁴³ The actinide–cobalt bond length is 3.0771(5) Å for **1.6** and 3.0319(7) Å for **1.7**. The sum of the covalent radii for thorium and cobalt and uranium and cobalt are 2.86 Å and 2.81 Å, respectively.⁴⁴ While longer than expected, the U–Co distance is within the range of limited examples present in the literature (2.9450(9) Å and 3.0812(7)–2.874(3) Å);^{24,45} there is no data to compare with in the case of Th–Co. The difference in bond lengths between **1.6** and **1.7** is consistent with the disparity in radii (either ionic or covalent) between thorium and uranium.

Interestingly, one of the cis carbonyls in each complex is tilted slightly towards the actinide center. The interaction, which does not appear to be a crystal packing effect, is more pronounced in the thorium example as indicated by both the Co–C2 (1.742(4) Å and 1.750(7) Å) and An–C2 (3.094(4) Å and 3.198(1) Å) distances in **1.6** and **1.7**, respectively, perhaps reflecting simply the difference in radii. Similar behavior has been observed for related carbonyl complexes with early transition metals.^{37,46}

Chapter 1

Table 1.2. Crystal and Refinement Data for Complexes **1.2–1.7**

Complex	1.2	1.3	1.4	1.5	1.6	1.7
Formula	C ₃₉ H ₆₀ ClN ₄ P ₃ Th	C ₃₉ H ₆₀ ClN ₄ P ₃ U	C ₄₃ H ₆₀ CoN ₄ O ₄ P ₃ Th	C ₄₃ H ₆₀ CoN ₄ O ₄ P ₃ U	C ₄₂ H ₆₀ CoN ₄ O ₃ P ₃ Th	C ₄₂ H ₆₀ CoN ₄ O ₃ P ₃ U
Molecular weight	945.33	951.32	1080.85	1086.84	1052.84	1058.83
Space Group	P-1	P-1	P-1	Pna2(1)	P-1	P-1
<i>a</i> (Å)	11.5293(10)	13.5354(4)	11.2506(14)	23.0608(9)	11.0757(7)	14.0553(4)
<i>b</i> (Å)	12.2573(10)	16.0795(3)	15.9358(19)	14.0118(6)	14.0911(8)	18.7308(5)
<i>c</i> (Å)	16.7699(14)	33.6127(8)	29.701(4)	14.0919(6)	18.7140(11)	22.2945(6)
<i>a</i> (°)	94.757(4)	95.0190(10)	82.195(6)	90	80.318(2)	73.8300(10)
<i>b</i> (°)	101.488(4)	97.5550(10)	83.056(6)	90	74.876(2)	89.0240(10)
<i>g</i> (°)	115.104(4)	106.0330(10)	83.218(6)	90	89.511(3)	80.5410(10)
<i>V</i> (Å ³)	2065.3(3)	6910.9(3)	5209.0(11)	4553.4(3)	2777.4(3)	5558.0(3)
<i>Z</i>	2	8	2	4	2	2
ρ_{calcd} (g/cm ³)	1.520	1.371	1.437	1.585	1.259	1.431
<i>F</i> ₀₀₀	948	2856	2220	2168	1052	2412
μ (mm ⁻¹)	3.822	3.713	3.332	4.066	3.092	3.337
Refl'ns collected	27508	91757	71236	15382	52419	99217
Indep. refl'ns	7520	24987	19981	6108	10197	20479
<i>R</i> _{int}	0.0902	0.1087	0.0536	0.0905	0.0312	0.0521
<i>R</i> ₁ , <i>wR</i> ₂	0.0470, 0.0666	0.0547, 0.0984	0.0423, 0.0715	0.0479, 0.1112	0.0304, 0.0716	0.0439, 0.0937
<i>R</i> ₁ , (all data)	0.0766	0.1070	0.0659	0.0654	0.0357	0.0598
GoF	1.006	0.927	1.039	0.955	1.039	1.057
Res. peak/hole (e ⁻ / Å ³)	0.985/-0.922	0.972/-1.479	1.467/-1.255	2.945/-1.435	1.689/-0.859	2.477/-2.785

NMR Spectroscopy. The thorium complex **1.2** shows a ^1H NMR spectrum indicative of three-fold symmetry in solution (assignments were confirmed by phosphorous decoupled and proton-proton COSY NMR). However, unlike the analogous Al and Cr compounds of the N_4P_3 ligand,²⁴⁻²⁶ the methylene protons are diastereotopic, appearing as two doublets at 3.89 ($J = 12$ Hz) and 3.23 ($J = 12$ Hz) ppm. Additionally, all proton peaks show coupling to phosphorous, a feature that appears unique to the actinide compounds (Figure 1.9b and 1.9c). The ^{31}P NMR further confirms the three-fold symmetry, with a single resonance at 4.83 ppm. While the ^1H NMR spectrum for **1.3** is broad, paramagnetically shifted, and lacking any coherent splitting, the number of signals is in agreement with the symmetry observed in the thorium analogue. A phosphorous signal could not be detected, as is common in the presence of an f^2 uranium center (see below).²⁴

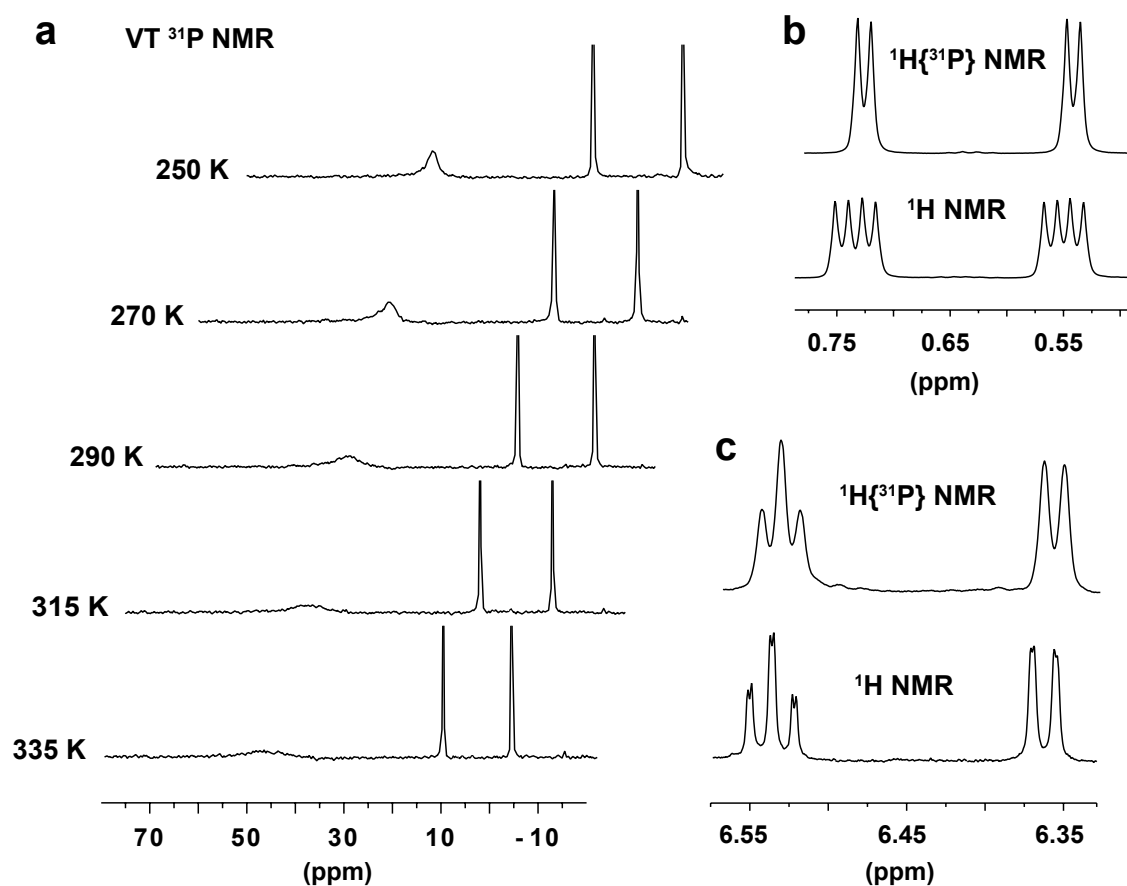


Figure 1.9. a) Variable temperature ^{31}P NMR spectra of complex **1.6**. b) $^1\text{H}\{^{31}\text{P}\}$ (top) and ^1H NMR (bottom) spectra of two methyl groups of complex **1.4**. c) $^1\text{H}\{^{31}\text{P}\}$ (top) and ^1H NMR (bottom) spectra of two aromatic protons of complex **1.2**. Both b and c illustrate the unique effect of phosphorus coupling observed in the ^1H NMR of the series.

Much like the starting chloride complex **1.2**, the solution state behavior of the thorium isocarbonyl **1.4** is indicative of three-fold symmetry, with the ^1H NMR resonances resembling those seen for **1.2**. The methylene protons remain diastereotopic at 3.55 ($J = 12$ Hz) and 3.05 ppm ($J = 12$ Hz), respectively, again likely a result of phosphine coordination to the thorium center. There is a single ^{31}P NMR peak that is shifted from 4.83 ppm for **1.2** to 6.41 ppm for **1.4**, indicating a small deshielding effect, presumably due to a slightly stronger interaction of the actinide center with the carbonyl ligand. Similar to complex **1.3**, the ^1H NMR spectrum for **1.5** is broad, paramagnetically shifted, and lacks coherent splitting, but the number of signals is in agreement with the symmetry observed in the thorium analogue. Likewise, the ^{31}P spectrum is featureless due to paramagnetism.

The solution state behavior of the metal–metal bonded species **1.6** proves more complicated than either precursor, but upon careful inspection reflects the coordination seen in the solid state. The three-fold symmetry observed in thorium compounds **1.2** and **1.4** is absent for **1.6**. Instead, NMR spectroscopy indicates a loss of symmetry resulting from the coordination of a phosphine arm to the cobalt center upon loss of CO. Where there had previously been only one resonance per proton group (i.e. aromatic, methylene, methine and isopropyl) in compounds **1.2** and **1.4**, three signals are observed in **1.6**. Accordingly, there are three signals in the ^{31}P NMR at 44.59, 9.43 and -6.59 ppm. The downfield resonance is broad, but in good agreement with phosphorous shifts reported for similar cobalt compounds.^{37,47} Variable temperature experiments reveal a further broadening of the signal at higher temperatures and a sharpening at low temperatures (Figure 1.9a). Given the shift, and the dissimilarity from the other two signals, it seems likely that the broad signal corresponds to a cobalt-bound phosphine. The fluxional behavior could be due to an exchange of the ligand between the cobalt and the thorium, or the result of a Berry pseudorotation involving the carbonyls. Inequivalence of the remaining phosphorous atoms reflects the two different chemical environments observed in the solid-state structure. The features of the ^1H and ^{31}P NMR spectra for complex **1.7** are analogous to those described for paramagnetic complexes **1.3** and **1.5**, with the exception that, like complex **1.6**, the asymmetry of **1.7** results in a tripling of the peaks.

Infrared Spectroscopy. In addition to providing a facile platform for exploring photolytic chemistry, the carbonyls of complexes **1.4–1.7** also supply a useful spectroscopic handle to examine structural aspects of this series. Solid-state IR spectra of compounds **1.4** and **1.5** show two sharp CO stretches (Table 1.3) consistent with the approximate C_{3v} symmetry of the cobalt fragment seen in the crystal structures. Additionally, there is a broad stretch for the bridging carbonyls of **1.4** and **1.5** at 1732 and 1748 cm^{-1} , respectively. The dramatic weakening in the energy of this stretch is consistent with the electronic redistribution required to form the bridge, and is similar to the few examples reported for actinides mentioned previously. The terminal CO stretches observed for **1.4** and **1.5** are significantly lower in energy than those seen in the cobalt starting material, indicating a significant redistribution of negative charge throughout the $[\text{Co}(\text{CO})_4]^-$ unit via cobalt-carbonyl backbonding. This is also reflected in the expanding and contracting respectively of the C–O and Co–C distances of the end on carbonyl groups, as well as the C4–O4 and Co–O4 values of the isocarbonyl (Table 1.1).

Table 1.3. Selected FTIR Data for Complexes **1.4–1.7** and Related Compounds^a

Compound	ν_{CO} (cm ⁻¹)
Free CO	2143
Na[Co(CO) ₄]	2024, 1878
1.4	2016, 1923, 1732
1.5	2013, 1922, 1748
1.6	1978, 1905, 1858
1.7	1977, 1907, 1864

^aCollected as Nujol mulls between KBr plates

Electronic redistribution is also evident in the solid-state IR spectra of compounds **1.6** and **1.7**, which show three sharp CO stretches consistent with the geometry and CO coordination number to the cobalt unit seen in the crystal structure. The CO stretch of the carbonyl trans to the metal–metal bond (1858 and 1864 cm⁻¹ for **1.6** and **1.7**, respectively) provides a probe of the interaction strength and is indeed the only stretch with a significant disparity between the two complexes.³⁷ The strength of the carbonyl stretch should be affected by the bonding in the An–Co–C–O linkage. The stronger the An–Co interaction, the weaker the Co–CO backbonding, and hence the stronger C–O stretching frequency. The C–O stretch of **1.7** has a higher frequency than **1.6**, indicating the U–Co interaction is stronger than that of the Th–Co. Additionally, the stretches for **1.6** and **1.7** are weaker than for those of their isocarbonyl counterparts, consistent with a polarization of charge from the cobalt to the actinide center and a corresponding decrease in Co–CO backbonding.

Magnetic Susceptibility. As an additional means of evaluating the electronic structure of the uranium series, variable temperature magnetic susceptibilities (χ) of complexes **1.3**, **1.5** and **1.7** were measured in the solid state (Figure 1.10). The effective magnetic moments of **1.3**, **1.5** and **1.7** at 300 K are 2.6, 2.7, and 3.2 Bohr magnetons (μ_{B}), respectively. This value is lower than the free ion magnetic moments of both U(III) and U(IV), which is 3.6 μ_{B} in both cases.⁴⁸ Both crystal field splitting and covalency can affect the magnetic moment, making the room temperature moment alone insufficient in determining the uranium oxidation state. The observed values are similar to those reported for both U(III) and U(IV) amide complexes.^{48–53}

For **1.3**, **1.5** and **1.7**, μ_{eff} decreases toward zero as the temperature is lowered, which is consistent with U(IV), with an f^2 , ³H₄ configuration and a singlet ground state.¹ The temperature independent ground state is indicated in the χ vs. T plot by a change in slope (indicated with vertical arrows in Figure 1.10) where the first excited state becomes thermally populated. In **1.5**, the ground state is least magnetic and is the only appreciably populated state up to ~100 K. In **1.3**, the ground state has a greater magnetic susceptibility and persists to a somewhat lower temperature, ~70 K. In **1.7**, the ground state has the greatest magnetic susceptibility and persists to ~60 K.

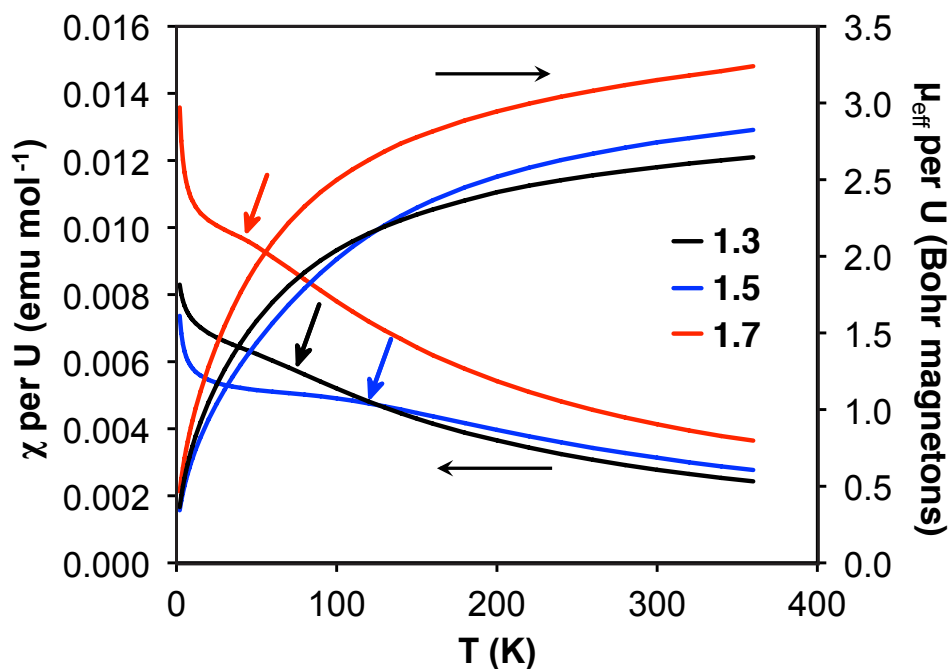


Figure 1.10. Variable-temperature magnetic susceptibility of complexes **1.3**, **1.5** and **1.7**. Note: vertical arrows indicate the change in slope due to thermal population of the first excited state.

Both the magnetic susceptibility of the singlet state and the temperature over which this state is exclusively occupied are functions of the strength of the crystal field. Stronger ligands lead to larger splitting between the ground state and higher lying states, decreasing the susceptibility of the ground state and increasing the temperature over which it is solely occupied. The splitting of the $^3\text{H}_4$ state is greatest in **1.5** and smallest in **1.7**. This mirrors the bond distances observed between the uranium center and the apical ligand, with the shortest (U–OC) in **1.5** and longest (U–Co) in **1.7**. In agreement with the crystallographic and NMR data presented previously, this suggests that the isocarbonyl displays the strongest interaction with the U(IV) center and that Co has the weakest. This in turn underscores the necessity to employ photolytic excitation to enable the formation of the An–Co bond via ligand exchange.

UV-vis/NIR Spectroscopy. Finally, the electronic structure of the uranium series was investigated using UV-vis/NIR spectroscopy (Figure 1.11). Complexes **1.3**, **1.5** and **1.7** display a broad shoulder at ~300 nm, followed by a peak at ~430 nm, showing shifts in agreement with the gradual orange-to-red color change observed across the series. Both peaks are similar to those reported for the analogous Al and Cr compounds of the ligand and are consistent with π – π^* transitions in the ligand backbone and M–L charge transfer, respectively.^{25–27} Additionally, there are several sharp peaks not seen in the main group or transition metal compounds at ~675 nm ($\epsilon = \sim 1.25 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$), consistent with f -based transitions.

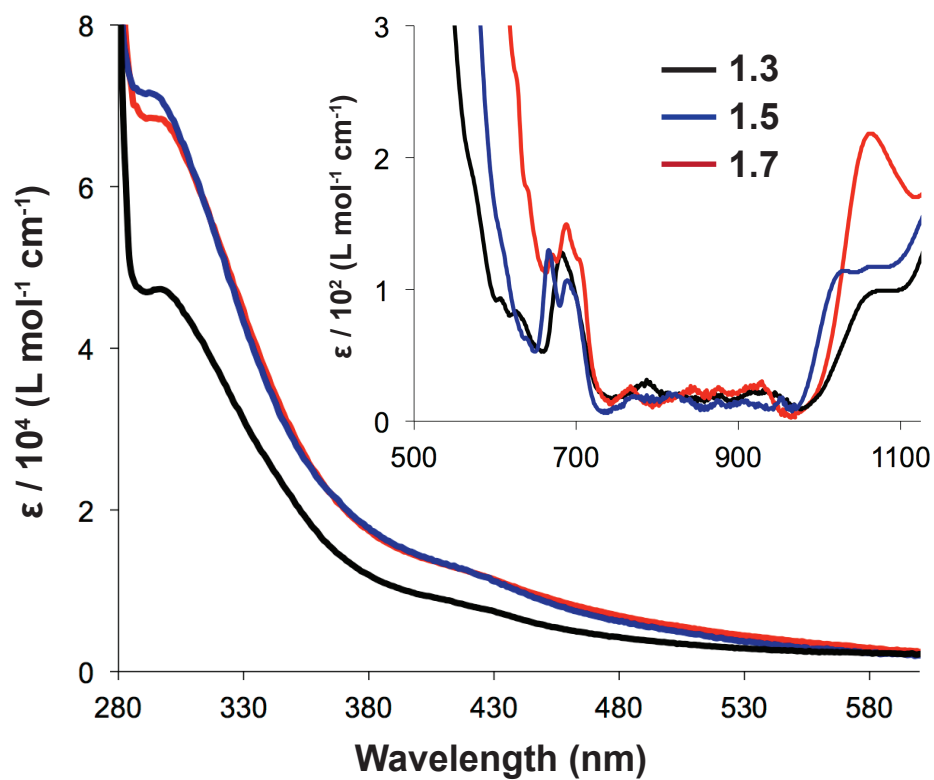


Figure 1.11. UV–visible absorption spectra of complexes **1.3**, **1.5** and **1.7** in toluene. Inlay: NIR absorption spectra of complexes **1.3**, **1.5** and **1.7** in toluene.

In contrast to the UV–vis region, the broad peaks in the NIR spectra are distinct between compounds. The uranium chloride complex **1.3** displays a single peak at 1064 nm ($\epsilon = 0.97 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$), similar to that reported for the aluminum–cobalt complex. However, the isocarbonyl complex **1.5** displays two peaks at 1024 nm ($\epsilon = 1.12 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$) and 1056 nm ($\epsilon = 1.17 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$), and the U–Co bound complex **1.7** displays a more intense single peak at 1058 nm ($\epsilon = 2.16 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$). Metal-based transitions were observed in the NIR region for the corresponding main group and transition metal examples of this ligand. Likewise, the two peaks observed for isocarbonyl **1.5** may arise due to independent cobalt and uranium based transitions. Subsequently, and consistent with a polarization of charge between the metal centers in **1.7**, a single transition of increased intensity is seen upon formation of the U–Co bond.

Conclusions

Our studies have shown that actinide–transition metal bonds can be formed via photolysis of heterobimetallic isocarbonyl complexes. A key design feature of this work is the ready availability of a pendent phosphine ligand that is unique to the N_4P_3 ligand scaffold. The secondary coordination sphere incorporated into this ligand framework is crucial to the formation of actinide–metal bonds upon photolysis since without it the resulting coordinatively unsaturated $Co(CO)_3$ complex would likely decompose. In this way, we have generated two new An–Co complexes, including one featuring a previously unknown Th–Co bond. Additionally, this series of complexes provides useful information about the coordination environments, oxidation states and bonding of what is a relatively limited number of low-valent actinide compounds. We believe this approach represents a new way to create actinide–metal bonds and may yield a rich platform for expanding the study of actinide metal–metal bonding and associated reactivity. Proposals for the expansion of this chemistry are presented in the Future Directions chapter.

Experimental Details

General procedures. Unless otherwise noted, all reactions were performed using standard Schlenk line techniques, or in an MBraun N₂-atmosphere glovebox (<1 ppm O₂/H₂O). All glassware and Celite were stored in an oven at ~150 °C. Dimethoxyethane (DME), diethyl ether (Et₂O), toluene, hexanes, pentane and pyridine were dried and degassed using a Phoenix Solvent Drying System commercially available from JC Meyer Solvent Systems. Hexamethyldisiloxane (HMDSO) was vacuum-transferred from CaH₂ and degassed by bubbling N₂ through the solution. Deuterated solvents were vacuum-transferred from either sodium/benzophenone (C₆D₆ and toluene-*d*₈) or CaH₂ (pyridine-*d*₅) and degassed with three freeze–pump–thaw cycles. All NMR spectra were recorded at the specified temperature on Bruker AVQ-400, DRX 500 or AV-600 spectrometers. Temperature calibration was performed using changes in chemical shift separation of ethylene glycol at high temperature, and methanol at low temperature. ¹H chemical shifts (δ) were calibrated using residual solvent peaks. ³¹P chemical shifts (δ) were referenced to an external standard (Ph₃PO at 23 ppm). UV–visible and near infrared (NIR) spectra were collected in toluene and determined with a UV-3101PC scanning spectrophotometer, using a Schlenk-adapted 1 mm quartz cell. Infrared (IR) spectra were recorded with a Thermo Scientific Nicolet iS10 FTIR spectrophotometer as Nujol mulls between KBr plates. Melting points were determined on an Optmelt SRS using sealed capillaries prepared under nitrogen and are uncorrected. Photolysis was conducted using a Rayonet reactor (Model RPR-100) centered at 253 nm with approximately 1.65 x 10¹⁶ photons/sec/cm³. The ligand N[*o*-(NCH₂PⁱPr₂)C₆H₄]₃,²⁴ ThCl₄(DME)₂,²⁸ UCl₄,²⁹ and Na[Co(CO)₄]⁵⁴ were prepared according to literature procedures.

K₃{N[*o*-(NCH₂PⁱPr₂)C₆H₄]₃} (1.1). A solution of the ligand N[*o*-(NCH₂PⁱPr₂)C₆H₄]₃ (2.0 g, 2.9 mmol) in toluene (40 mL) was added to a suspension of K[N(TMS)₂] (1.9 g, 9.7 mmol) in toluene (40 mL) to produce a yellow solution. The reaction mixture was stirred for 1 d, resulting in the precipitation of a yellow solid. The reaction mixture was filtered and washed with hexanes (2 × 5 mL) to afford the desired product as a pale yellow solid (2.33 g, 99% yield). ¹H NMR (400 MHz, pyridine-*d*₅, 293 K): δ 7.24 (d, 1H, Ar-*H*, *J* = 8.0 Hz), 7.04 (t, 1H, Ar-*H*, *J* = 8.0 Hz), 6.47 (d, 1H, Ar-*H*, *J* = 8.0 Hz), 5.93 (t, 1H, Ar-*H*, *J* = 8.0 Hz), 3.42 (ABq, 2H, CH₂, Δδ_{AB} = 0.13, *J*_{AB} = 16 Hz), 1.77 (m, 2H, CH), 1.11 (m, 12H, CH₃). ³¹P NMR (400 MHz, pyridine-*d*₅): δ 2.00. Mp: dec. > 164 °C.

{N[*o*-(NCH₂PⁱPr₂)C₆H₄]₃}ThCl (1.2). A solution of **1.1** (1.1 g, 1.4 mmol) in pyridine (25 mL) was added to a suspension of ThCl₄(DME)₂ (766 mg, 1.4 mmol) in pyridine (25 mL) to produce an off white suspension. The reaction mixture was stirred for 12 h, resulting in a pale yellow solution. The solvent was removed in vacuo to yield a pale orange solid. The solid was extracted with Et₂O (3 × 10 mL), filtered, and concentrated until saturation. Hexanes were added dropwise until cloudy and the solution was then chilled for 2 d at -40 °C to afford the product as colorless needles (843 mg, 65% yield). Single crystals suitable for X-ray diffraction were obtained from a concentrated solution of **1.2** in pentane stored at -40 °C for 12 hr. ¹H NMR (600 MHz, C₆D₆, 293 K): δ 7.18 (t, partially obscured by solvent, 1H, Ar-*H*, *J* = 6.0 Hz), 7.07 (d, 1H, Ar-*H*, *J* = 12 Hz), 6.53 (t, 1H, Ar-*H*, *J* = 9.0 Hz), 6.36 (d, 1H, Ar-*H*, *J* = 6.0 Hz), 3.89 (d, 1H, CH₂, *J* = 12 Hz), 3.23 (d, 1H, CH₂, *J* = 12 Hz), 2.06 (sept, 1H, CH, *J* = 6.0 Hz),

1.57 (sept, 1H, CH, $J = 6.0$ Hz), 1.27 (d, 3H, CH₃, $J = 6.0$ Hz), 1.24 (d, 3H, CH₃, $J = 6.0$ Hz), 0.84 (d, 3H, CH₃, $J = 6.0$ Hz), 0.66 (d, 3H, CH₃, $J = 6.0$ Hz). ³¹P NMR (600 MHz, C₆D₆, 293 K): δ 4.83. Anal. Calcd (%) for C₃₉H₆₀ClN₄P₃Th: C, 49.55; H, 6.40; N, 5.93. Found: C, 49.17; H, 6.69; N, 5.82. Mp: dec. > 138 °C.

{N[*o*-(NCH₂PⁱPr₂)C₆H₄]₃}UCl (1.3). A solution of **1.1** (1.0 g, 1.3 mmol) in pyridine (25 mL) was added to a suspension of UCl₄ (480 mg, 1.3 mmol) in pyridine (25 mL) to produce a red suspension. The reaction mixture was stirred for 12 h, resulting in a dark red solution. The solvent was removed in vacuo to yield a dark orange solid. The solid was extracted with Et₂O (3 × 10 mL), filtered, and concentrated until saturation. Hexanes were added dropwise until cloudy and the solution was then chilled for 1 d at -40 °C to afford the product as orange needles (807 mg, 68% yield). Single crystals suitable for X-ray diffraction were obtained from a concentrated solution of **3** in pentane stored at -40 °C for 12 h. ¹H NMR (400 MHz, C₆D₆, 293 K): δ 37.92 (s, br), 22.49 (s, br), 11.58 (s, br), 10.91 (s, br), 9.41 (s, br), 8.67 (m, br), 7.03 (s, br), 5.65 (s, br), 1.22 (m, br), -2.70 (s, br), -4.82 (s, br), -6.64 (s, br). UV-vis/NIR [nm, ϵ (M⁻¹ cm⁻¹): 298, 47,100; 431, 7,320; 680, 129; 1064, 97. Anal. Calcd (%) for C₃₉H₆₀ClN₄P₃U: C, 49.23; H, 6.36; N, 5.89. Found: C, 49.34; H, 6.45; N, 6.01. Mp: dec. > 145 °C. $\mu_{\text{eff}} = 2.6 \mu_{\text{B}}$ at 300 K.

{N[*o*-(NCH₂PⁱPr₂)C₆H₄]₃}Th(μ -OC)Co(CO)₃ (1.4). A solution of **1.2** (100 mg, 0.10 mmol) in toluene (2 mL) was added to a suspension of Na[Co(CO)₄] (21 mg, 0.10 mmol) in toluene (2 mL) to produce a pale yellow suspension. The reaction mixture was stirred for 12 h, resulting in a yellow solution and a fine white precipitate. The solvent was removed in vacuo to yield an off-white solid. The solid was extracted with toluene (3 × 2 mL), filtered, and concentrated until saturation. Hexanes were added dropwise until cloudy and the solution was then chilled for 1 d at -40 °C to afford the product as colorless blocks (88 mg, 77% yield). Single crystals suitable for X-ray diffraction were obtained from a concentrated solution of **1.4** in toluene stored at -40 °C for 12 h. ¹H NMR (600 MHz, C₆D₆, 293 K): δ 7.08 (t, 1H, Ar-*H*, $J = 9.0$ Hz), 7.02 (d, 1H, Ar-*H*, $J = 6.0$ Hz), 6.51 (t, 1H, Ar-*H*, $J = 9.0$ Hz), 6.11 (d, 1H, Ar-*H*, $J = 6.0$ Hz), 3.55 (d, 1H, CH₂, $J = 12$ Hz), 3.05 (d, 1H, CH₂, $J = 12$ Hz), 2.15 (sept, 1H, CH, $J = 6.0$ Hz), 1.46 (sept, 1H, CH, $J = 6.0$ Hz), 1.31 (d, 3H, CH₃, $J = 6.0$ Hz), 1.28 (d, 3H, CH₃, $J = 6.0$ Hz), 0.77 (d, 3H, CH₃, $J = 6.0$ Hz), 0.59 (d, 3H, CH₃, $J = 6.0$ Hz). ³¹P NMR (600 MHz, C₆D₆, 293 K): δ 6.41. IR (cm⁻¹): 2016 (m, CO), 1923 (s, CO), 1733 (s, CO), 1586 (m), 1310 (m), 1290 (m), 1234 (w), 1157 (w), 1116 (w), 1040 (w), 745 (m), 722 (m), 563 (m), 512 (m). Anal. Calcd (%) for C₄₃H₆₀CoN₄O₄P₃Th: C, 47.78; H, 5.60; N, 5.18. Found: C, 35.29; H, 3.63; N, 5.09. The isocarbonyl compounds are subject to very rapid thermal and photolytic decomposition unless kept frozen and in a dark environment. Therefore it is unsurprising that the found percentages for elemental analysis are not in good agreement. Mp: dec. > 136 °C.

{N[*o*-(NCH₂PⁱPr₂)C₆H₄]₃}U(μ -OC)Co(CO)₃ (1.5). A solution of **1.3** (330 mg, 0.34 mmol) in toluene (2 mL) was added to a suspension of Na[Co(CO)₄] (66 mg, 0.34 mmol) in toluene (2 mL) to produce an orange suspension. The reaction mixture was stirred for 12 h, resulting in a red solution and a fine white precipitate. The solvent was removed in vacuo to yield an orange solid. The solid was extracted with toluene (3 × 2 mL), filtered, and concentrated until saturation. Hexanes were added dropwise until cloudy and the solution was then chilled for 1 d at -40 °C to afford the product as orange blocks (281 mg, 76% yield). Single crystals suitable for X-ray diffraction were obtained from a concentrated solution of **1.5** in toluene stored at -40

$^{\circ}\text{C}$ for 12 h. ^1H NMR (400 MHz, C_6D_6 , 293 K): δ 52.86 (s, br), 23.92 (s, br), 16.58 (s, br), 12.66 (m, br), 10.29 (s, br), 8.39 (m, br), 8.31 (s, br), 3.44 (m, br), 0.29 (s, br), -2.04 (m, br), -3.13 (s, br), -12.93 (s, br). IR (cm^{-1}): 2013 (m, CO), 1922 (s, CO), 1748 (s, CO), 1586 (m), 1310 (m), 1290 (m), 1234 (w), 1157 (w), 1116 (w), 1049 (w), 747 (m), 722 (m), 560 (m), 517 (m). UV-vis/NIR [nm, ϵ ($\text{M}^{-1} \text{cm}^{-1}$)]: 296, 71,100; 429, 13,100; 668, 127; 693, 104; 1024, 112; 1056, 117. Anal. Calcd (%) for $\text{C}_{43}\text{H}_{60}\text{CoN}_4\text{O}_4\text{P}_3\text{U}$: C, 47.52; H, 5.56; N, 5.16. Found: C, 41.34; H, 3.86; N, 4.83. Mp: dec. $> 149^{\circ}\text{C}$. $\mu_{\text{eff}} = 2.7 \mu_{\text{B}}$ at 300 K.

$\{\text{N}[\sigma\text{-(NCH}_2\text{P}^i\text{Pr}_2)\text{C}_6\text{H}_4]_3\}\text{ThCo(CO)}_3$ (1.6**).** A solution of **1.4** (130 mg, 0.12 mmol) in toluene (2 mL) was irradiated with ultraviolet light (centered at 254 nm) for 12 h, resulting in a color change from pale yellow to yellow. The solvent was removed in vacuo to yield a pale yellow solid. The solid was extracted with Et_2O (3×2 mL), filtered, and concentrated until saturation. The solution was then chilled for 1 d at -40°C to afford the product as colorless blocks (79 mg, 61% yield). Single crystals suitable for X-ray diffraction were obtained by vapor diffusion at -40°C of hexane into a concentrated solution of **1.6** in toluene. ^1H NMR (600 MHz, C_6D_6 , 293 K): δ 7.23 (t, 1H, Ar- H , $J = 6.0$ Hz), 7.19 (t, 1H, Ar- H , $J = 6.0$ Hz), 7.12 (m, 2H, Ar- H), 7.06 (d, 1H, Ar- H , $J = 6.0$ Hz), 6.95 (d, 1H, Ar- H , $J = 6.0$ Hz), 6.61 (m, 2H, Ar- H), 6.52 (t, 1H, Ar- H , $J = 6.0$ Hz), 6.49 (t, 1H, Ar- H , $J = 6.0$ Hz), 6.42 (d, 1H, Ar- H , $J = 6.0$ Hz), 6.14 (d, 1H, Ar- H , $J = 6.0$ Hz), 4.38 (d, 1H, CH_2 , $J = 12$ Hz), 3.97 (d, 1H, CH_2 , $J = 12$ Hz), 3.62 (d, 1H, CH_2 , $J = 12$ Hz), 3.36 (m, 2H, CH_2), 3.14 (d, 1H, CH_2 , $J = 12$ Hz), 2.43 (sept, 1H, CH , $J = 6.0$ Hz), 2.00 (sept, 1H, CH , $J = 6.0$ Hz), 1.87 (m, 2H, CH), 1.77 (sept, 1H, CH , $J = 6.0$ Hz), 1.57 (sept, 1H, CH , $J = 6.0$ Hz), 1.43 (d, 3H, CH_3 , $J = 12$ Hz), 1.39 (d, 3H, CH_3 , $J = 6.0$ Hz), 1.27 (d, 3H, CH_3 , $J = 6.0$ Hz), 1.11 (d, 3H, CH_3 , $J = 6.0$ Hz), 0.94 (m, 9H, CH_3), 0.86 (d, 3H, CH_3 , $J = 6.0$ Hz), 0.81 (d, 3H, CH_3 , $J = 12$ Hz), 0.74 (d, 3H, CH_3 , $J = 6.0$ Hz), 0.62 (m, 6H, CH_3). ^{31}P NMR (600 MHz, C_6D_6 , 293 K): δ 44.59, 9.43, -6.59. IR (cm^{-1}): 1979 (s, CO), 1905 (s, CO), 1858 (s, CO), 1591 (m), 1310 (m), 1290 (m), 1254 (w), 1156 (w), 1117 (w), 1040 (w), 856 (w), 743 (m), 727 (m). Anal. Calcd (%) for $\text{C}_{42}\text{H}_{60}\text{CoN}_4\text{O}_3\text{P}_3\text{Th}$: C, 47.91; H, 5.74; N, 5.32. Found: C, 48.04; H, 5.86; N, 5.19. Mp: dec. $> 160^{\circ}\text{C}$.

$\{\text{N}[\sigma\text{-(NCH}_2\text{P}^i\text{Pr}_2)\text{C}_6\text{H}_4]_3\}\text{UCo(CO)}_3$ (1.7**).** A solution of **1.5** (150 mg, 0.14 mmol) in toluene (2 mL) was irradiated with ultraviolet light (centered at 254 nm) for 12 h, resulting in a color change from orange to red. The solvent was removed in vacuo to yield a red solid. The solid was extracted with Et_2O (3×2 mL), filtered, and concentrated until saturation. The solution was then chilled for 1 d at -40°C to afford the product as red blocks (87 mg, 58% yield). Single crystals suitable for X-ray diffraction were obtained from a concentrated solution of **1.7** in HMDSO stored at -40°C for 12 h. ^1H NMR (400 MHz, C_6D_6 , 293 K): δ 88.56 (s, br), 75.00 (s, br), 51.45 (s, br), 38.96 (s, br), 28.70 (s, br), 27.11 (s, br), 20.06 (s, br), 17.34 (s, br), 17.05 (s, br), 16.45 (s, br), 16.05 (s, br), 14.41 (s, br), 11.84 (s, br), 11.72 (s, br), 11.29 (m, br), 11.10 (m, br), 9.17 (s, br), 8.32 (s, br), 7.91 (s, br), 7.52 (s, br), 6.42 (s, br), 3.39 (m, br), 2.68 (m, br), 2.17 (s, br), -1.84 (s, br), -2.05 (m, br), -9.41 (m, br), -10.95 (s, br), -11.57 (s, br), -11.79 (s, br), -15.67 (s, br), -19.01 (s, br), -24.40 (s, br), -26.25 (s, br). IR (cm^{-1}): 1977 (s, CO), 1908 (s, CO), 1864 (s, CO), 1590 (m), 1310 (m), 1288 (m), 1253 (w), 1155 (w), 1117 (w), 1048 (w), 846 (w), 742 (m), 722 (m). UV-vis/NIR [nm, ϵ ($\text{M}^{-1} \text{cm}^{-1}$)]: 299, 69,800; 433, 10,900; 669, 124; 689, 149; 1058, 216. Anal. Calcd (%) for $\text{C}_{42}\text{H}_{60}\text{CoN}_4\text{O}_3\text{P}_3\text{U}$: C, 47.64; H, 5.71; N, 5.29. Found: C, 47.52; H, 5.79; N, 5.16. Mp: dec. $> 145^{\circ}\text{C}$. $\mu_{\text{eff}} = 3.0 \mu_{\text{B}}$ at 300 K.

Crystallographic procedures. X-ray structural determinations were performed at CHEXRAY, University of California, Berkeley, on a Bruker APEX II Quazar diffractometer. The instrument is Kappa Geometry with DX, and is a 3-circle diffractometer that couples a CCD detector⁵⁵ with a sealed-tube source of monochromatized Mo K α radiation. A crystal of appropriate size was coated in Paratone-N oil and mounted on a Kaptan loop. The loop was transferred to the diffractometer, centered in the beam, and cooled by a nitrogen flow low-temperature apparatus that had been previously calibrated by a thermocouple placed at the same position as the crystal. Preliminary orientation matrices and cell constants were determined by collection of 60 10 s frames, followed by spot integration and least-squares refinement. The reported cell dimensions were calculated from all reflections with $I > 10\sigma$. The data were corrected for Lorentz and polarization effects; no correction for crystal decay was applied. An empirical absorption correction based on comparison of redundant and equivalent reflections was applied using SADABS.⁵⁶ All software used for diffraction data processing and crystal-structure solution and refinement are contained in the APEX2 program suite (Bruker AXS, Madison, WI).⁵⁷ Thermal parameters for all non-hydrogen atoms were refined anisotropically. For all structures, $R1 = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$; $wR2 = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{1/2}$, ORTEP diagrams were created using the ORTEP-3 software package and POV-ray.^{58,59}

Magnetism procedures. Uranium complexes **1.3**, **1.5** and **1.7** (6.4 mg) were sandwiched between two plugs of quartz wool (Hereaus, 6.6 mg) in a 4 mm OD quartz tube, which was flame sealed on both ends. Sample magnetization was recorded at 0.1 T, 0.5 T, and 1 T using a Quantum Designs MPMS SQUID magnetometer. Magnetization was corrected for the diamagnetism of the quartz wool using Pascal's constants (no correction for the diamagnetism of the quartz tube is needed as the quartz tube never leaves the SQUID coils). Molar susceptibility was corrected for the presence of a small amount of ferromagnetic impurity (M_{ferro}), the diamagnetism of the quartz wool (χ_{QW}), ligands and uranium (χ_{dia}) using Pascal's constants, and calculated using the following equation:

$$\chi_{\text{mol}} = \frac{(\text{molecular weight})}{(\text{sample mass})} \left[\frac{(M_{\text{meas}} - M_{\text{ferro}})}{H} - \chi_{\text{QW}} \right] - \chi_{\text{dia}}$$

where χ_{mol} is the molar susceptibility, M_{meas} is the measured magnetization, M_{ferro} is the magnetization of the ferromagnetic impurity, which is temperature independent and assumed to be identical at all fields, χ_{QW} is the contribution to the susceptibility due to the quartz wool, χ_{dia} is the diamagnetic correction, and H is the applied field. For **1.3** and **1.5**, this equation was applied to the 0.5 T and 1 T data to determine, M_{ferro} , which was 1.6×10^{-5} emu and 2.92×10^{-5} emu, respectively. The 0.1 T data was fit to the other data using $M_{\text{ferro},0.1\text{T}} = 0.63 M_{\text{ferro}}$ because the 0.1 T data is below the anisotropy field of the ferromagnetic impurity (*see below*); the value of 0.63 was determined by fitting the 0.1 T data to the 0.5 T and 1 T data. For **1.7**, the amount of ferromagnetic impurity was determined using the 0.1 T, 0.5 T and 1 T data and $M_{\text{ferro},0.1\text{T}} = 0.63 M_{\text{ferro}}$; $M_{\text{ferro}} = 1.6 \times 10^{-5}$ emu.

Two ferromagnetic impurities are commonly encountered in laboratory samples, steel or iron metal and magnetite or other ferrites from oxide coating on stainless steel lab equipment. Of these, magnetite is far more likely to be encountered. In general, the magnetization of ferromagnets is temperature independent below the Curie temperature, which is 860 K for

magnetite, respectively, so magnetization of the impurity is temperature independent for this experiment. The magnetization of ferromagnets is also largely field-independent above the anisotropy field, which is approximately 0.2 T for magnetite, above which the magnetization is ~ 90 emu/g.⁶⁰ Below the anisotropy field, the magnetization of a magnet is roughly linear with applied field. Based on the assumption that the impurity is magnetite or some other ferrite resulting from the abrasion of stainless steel lab equipment, the data were corrected for a temperature and field independent ferromagnetic impurity. M_{ferro} was allowed to vary to minimize least squares difference between χ_{mol} at different fields, which produced a saturation magnetization of $M_{\text{ferro}} \sim 2 \times 10^{-5}$ emu, which corresponds to ~ 0.2 μg of magnetite.

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Chapter 1

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Chapter 2

Synthesis, Solution-Phase Studies and Solid-State Characterization of Thorium(IV) and Uranium(IV) Corrole Complexes

Overview

Since their synthesis as vitamin B₁₂ mimics in the early 1960's, corrole macrocycles have been used as ligands for many late transition metals. Corroles are non-innocent ligands and provide steric protection that allows them to stabilize a wide range of highly reactive species. As such, corroles have many synthetic, biochemical and materials applications. Recent work in our group has opened up more of the periodic table to be explored with the synthesis of a suitable salt metathesis reagent. The following chapter describes the synthesis and characterization of the first actinide corrole complexes. These compounds add to a limited number of actinide macrocyclic complexes and offer a unique opportunity to study their electronic structure and bonding and explore reactivity. Portions of this chapter have previously been published in: Ward, A. L., Buckley, H. L., Lukens, W. W., and Arnold, J. "Synthesis and Characterization of Thorium(IV) and Uranium(IV) Corrole Complexes." *J. Am. Chem. Soc.* **2013**, 135, 13965.

Introduction

The organometallic and coordination chemistry of actinide elements has become a subject of increasing interest over the past decade.¹⁻⁶ Despite this recent surge, the study of non-aqueous actinides remains underexplored when compared to that of the *s*, *p* and *d* block, or even lanthanides. A better understanding of the differences in covalency between the 4*f* and 5*f* elements, as well as actinide-ligand complex formation, has direct implications for improving nuclear waste remediation schemes.^{7,8} Additionally, actinides have access to a wide variety of oxidation states, and possess *f* orbitals capable of participating in bonding, allowing them to offer reactivity modes different from their better-studied transition metal and lanthanide counterparts. Recognition of these unique attributes has led to the discovery of actinide coordination compounds that facilitate small molecule activation,^{9,10} atom-transfer reactions^{11,12} and hydrocarbon functionalization,^{13,14} providing ample motivation for the development of both novel actinide systems and catalytic methodologies.^{15,16}

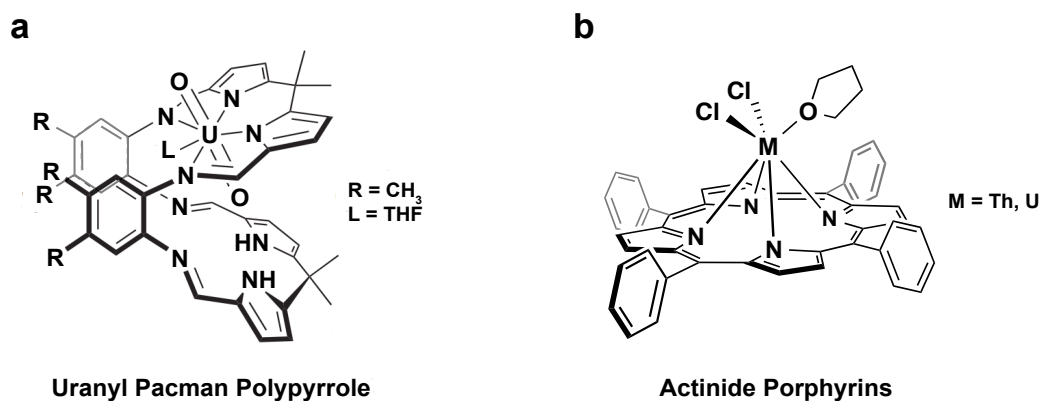


Figure 2.1. Macrocyclic actinide complexes. a) "Pacman" polypyrrole uranyl complex. b) Thorium and uranium porphyrin complexes.

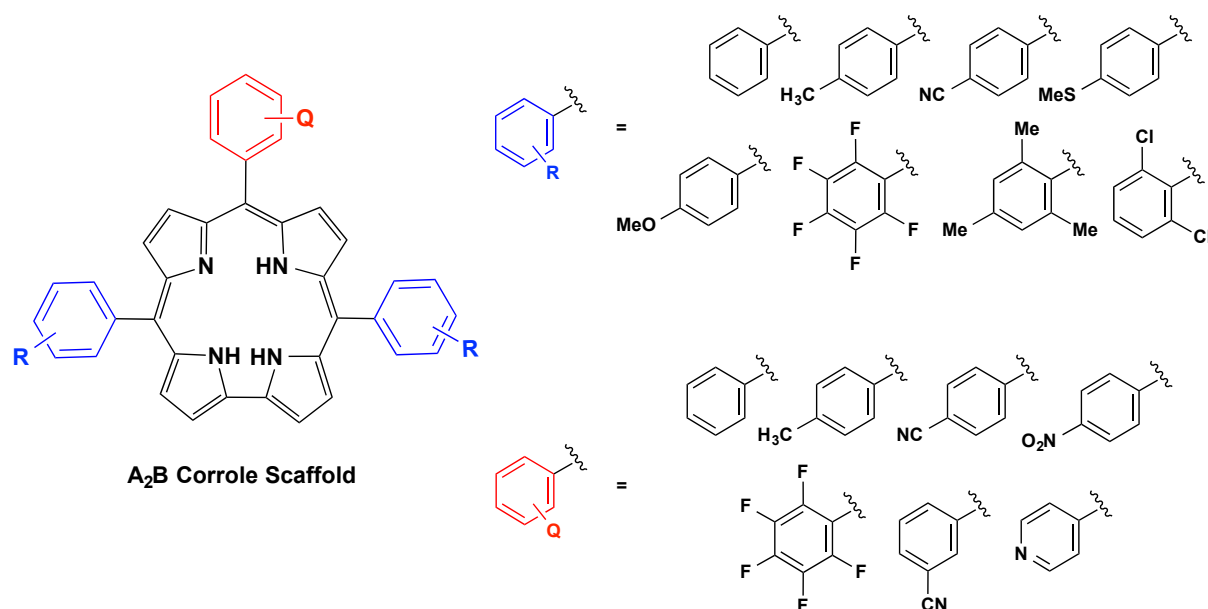


Figure 2.2. Corrole ligand with A₂B substitution and its readily accessible derivatives.

Due in large part to the kinetic and thermodynamic stability afforded via the macrocyclic effect,¹⁷ crown ethers,¹⁸ calixarenes¹⁹ and more recently “Pacman” polypyrroles²⁰ (Figure 2.1a) have been widely utilized for the study of *f*-element coordination chemistry and separation science. However, the vast majority of work focuses on macrocyclic complexes of the uranyl cation, with low valent actinide examples remaining largely absent.^{21,22} The few exceptions include the thorium²³ and uranium²⁴ porphyrins first reported in 1980’s (Figure 2.1b). Yet, in contrast to the plethora of *d*-element compounds, the actinide examples comprise a body of only nine structurally characterized (and thus far unreactive) complexes, highlighting the dearth of suitable low valent starting platforms.²⁵

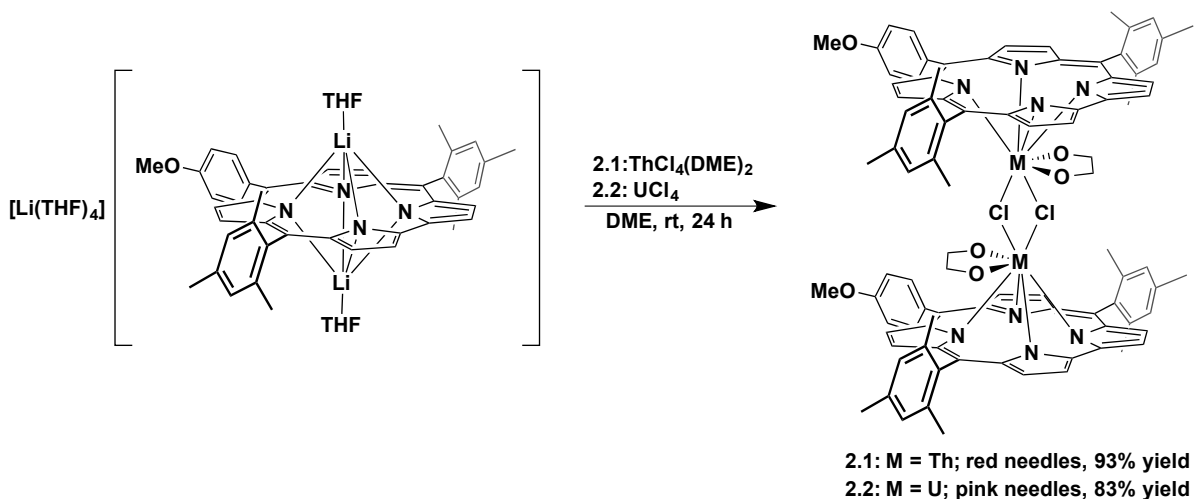
Corroles are close relatives of porphyrins; these tribasic, redox active, and strongly σ donating macrocycles stabilize metals in a wide variety of oxidation states. Two major advances in corrole chemistry have led to a recent expansion of the field. First, developments in the synthetic route to free-base corroles have led to much higher yields of the ligand, as well as access to a wider variety of derivatives.²⁶ This has allowed for a more straightforward entry into subsequent metal chemistry and greatly expanded the steric and electronic controls available via ligand tuning. Particularly relevant to this chapter are the A₂B corroles, which are a diverse subset of ligands (Figure 2.2). Secondly, since their initial synthesis, the chemistry of corroles has focused exclusively on mid- to late -transition metal complexes, but work in our group has led to the synthesis of a lithium corrole complex that has proven to be an effective salt metathesis reagent.²⁷ This has granted access to a much broader range of the periodic table for corroles and recently early transition metal and lanthanide derivatives have been reported.^{ref} Together, these breakthroughs have greatly expanded both the breadth and depth of corrole chemistry.

In addition to the tunability of the ligand itself, corroles present an N_4 ring for metal coordination smaller than that of porphyrins, leading to reactive systems by virtue of the out-of-plane nature of many metal ions, while still offering rigid steric protection along one face of the molecule.^{28,29} These systems have shown great promise with many mid- to late-transition metals over a wide variety of areas including catalysis, photochemical sensing, biomedicine and alternative energy applications.^{30,31} Exploiting these properties, in combination with the special features f -element metals afford, yields a novel starting platform for actinides that holds promise for a plethora of applications including the facilitation of actinide–actinide bonding, support of formally low valent Th(II) and U(II/III), single molecule magnetism and catalytic methodologies. Here, utilizing the aforementioned trithio corrole,²⁷ the synthesis and characterization of the first actinide corroles, featuring U(IV) and Th(IV) is discussed.

Results and Discussion

Synthesis and Structural Properties. The complexes, $(\text{Mes}_2(p\text{-OMePh})\text{corrole})_2\text{Th}_2(\mu\text{-Cl})_2(\text{DME})_2$ (**2.1**) and $(\text{Mes}_2(p\text{-OMePh})\text{corrole})_2\text{U}_2(\mu\text{-Cl})_2(\text{DME})_2$ (**2.2**), were synthesized via combination, in dimethoxyethane (DME), of the corresponding lithium corrole, $(\text{Mes}_2(p\text{-OMePh})\text{corrole})\text{Li}_3 \cdot 6\text{THF}$,³¹ with $\text{ThCl}_4(\text{DME})_2$ ³² and UCl_4 ,³³ respectively (Scheme 2.1). Both reactions were stirred at room temperature for 1 d, resulting in precipitation of a purple solid in the case of thorium complex **2.1**, while a dark red solution was observed for the uranium complex **2.2**. Evaporation of the solvent under vacuum, followed by crystallization from a mixture of dichloromethane (DCM) and hexanes, afforded dark red needles of **2.1** (93% yield), and dark pink needles of **2.2** (83% yield).

Scheme 2.1. Synthesis of Thorium(IV) Corrole **2.1** and Uranium(IV) Corrole **2.2**^a



^aMethyl groups of coordinated DME molecules have been omitted for clarity.

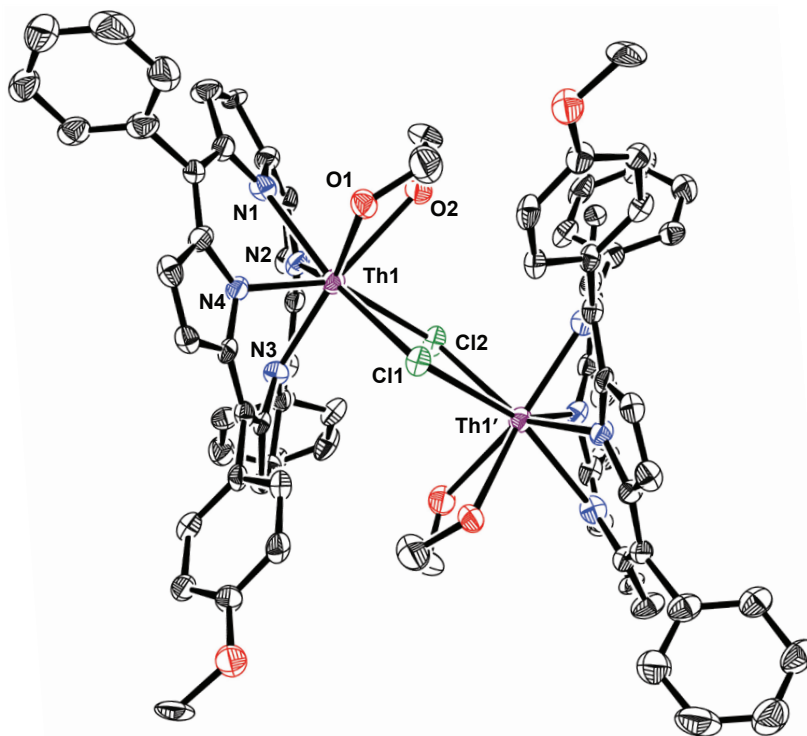


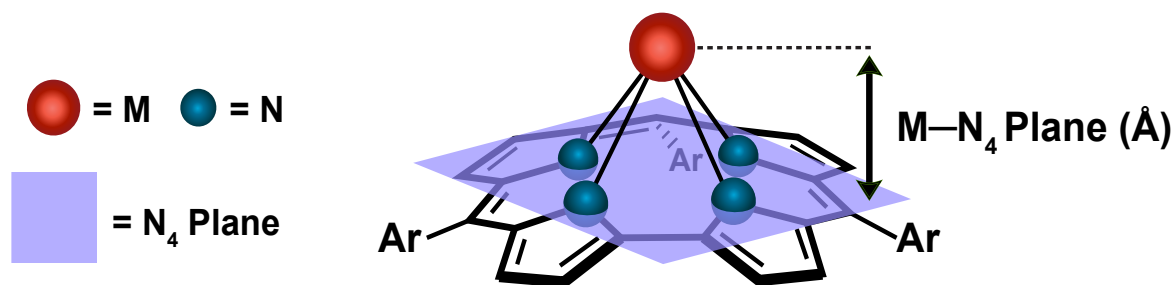
Figure 2.2. Molecular structure of thorium(IV) corrole **2.1**. Thermal ellipsoids are set to a 50% probability level. Hydrogen atoms, and both the mesityl and DME methyl groups, have been omitted for clarity.³⁹

Surprisingly, in comparison to related porphyrin and corrole complexes,^{23,24,34} both **2.1** and **2.2** crystallize as dimers, with two metal centers joined via bis(μ -chlorido) linkages. This type of structure is unprecedented in corrole chemistry, with the closest examples being the recently reported W and Mo μ -oxos,^{35,36} and is rare for actinides, particularly with sterically demanding ligands, due to the relatively weak nature of the M–Cl dative bond.^{37,38} Th(IV) corrole **2.1** is shown in ORTEP view in Figure 2.2; the structure of the U(IV) species is analogous (Figure 2.4). Each eight-coordinate metal atom is bound by a trianionic corrole, a bidentate DME ligand and two chlorides (additional crystallographic details are presented in Table 2.2). This is in contrast to the recently reported lanthanide corroles, as well as the actinide porphyrins, which are all monomeric.^{23,24,34}

Table 2.1. Selected Bond Lengths (Å) and Angles (°) for Complexes **2.1** and **2.2**

Complex	2.1	2.2
Bond Lengths (Å)		
M–N1	2.413(7)	2.313(6)
M–N2	2.394(5)	2.338(7)
M–N3	2.368(6)	2.293(6)
M–N4	2.356(4)	2.313(6)
M–Cl1	2.932(2)	2.873(2)
M–Cl2	2.886(1)	2.840(1)
M–O1	2.655(5)	2.659(6)
M–O2	2.586(5)	2.555(5)
M–M'	4.7279(4)	4.6621(5)
Bond Angles (°)		
N1–M–N2	64.2(2)	65.0(2)
N3–M–N4	75.7(2)	77.0(2)
N3–M–Cl1	93.91(1)	94.9(1)
O1–M–Cl1	71.9(1)	70.2(1)

The coordination geometry about the metal center is approximately dodecahedral, and both the metal-chloride (Th1–Cl1 2.932(2) Å and Th1–Cl2 2.886(1) Å; U1–Cl1 2.873(2) Å and U1–Cl2 2.840(1) Å) and metal-solvent (Th1–O1 2.665(5) Å and Th1–O2 2.586(5) Å; U1–O1 2.659(6) Å and U1–O2 2.555(5) Å) interactions are characteristic of those of other Th(IV) and U(IV) complexes.^{32,33,40–43} The Th1–Th1' distance of 4.7279(4) and U1–U1' distance of 4.6621(5) Å are similar to those reported for existing chloride diamond-core Th(IV) and U(IV) compounds.^{38,42–45} The average Th–N distance (2.39(1) Å) is longer than is typical for a Th–amido bond, but comparable to that of the thorium(IV) porphyrin (2.40 Å).²³ Likewise, the average U–N distance of 2.33(1) Å is slightly shorter than the analogous uranium(IV) porphyrin U–N distance at 2.41 Å.²⁴ As is expected given the smaller ionic radius of uranium, this is also slightly shorter than that of the Th–N corrole distance.

**Figure 2.3.** Diagram of the N₄ plane, as defined by the nitrogen atoms of the corrole.

The thorium center in **2.1** is located 1.403 Å above the N₄ plane (as defined by the nitrogen atoms of the corrole. See Figure 2.3), while the uranium of **2.2** is displaced by 1.330 Å. In **2.1**, the metal–plane distance is slightly shorter than for that of the thorium porphyrin (1.424 Å). In complex **2.2**, the opposite is true: the corresponding uranium porphyrin shows a value of 1.29 Å. The larger ring size of the porphyrin, difference in charge on the macrocycle (dianionic vs. trianionic), varying coordination number, and dimeric structure of corroles **2.1** and **2.2** (in contrast to the monomeric porphyrins), can all be considered as competing factors in determining this metric; nonetheless, the differences are not definitively rationalized based on the data available to date. Apart from one lanthanum corrole complex,³⁴ where the La–N₄ plane distance is 1.469 Å (and the aforementioned thorium porphyrin), the values of **2.1** and **2.2** are the largest metal–N₄ plane displacements for any reported macrocycle, with the next closest being the Bi corrole distance at 1.15 Å.⁴⁶ The fact that thorium and uranium are slightly closer to the corrole than the lanthanum is consistent with the difference in radii, both ionic and covalent, of the metals involved.^{47,48}

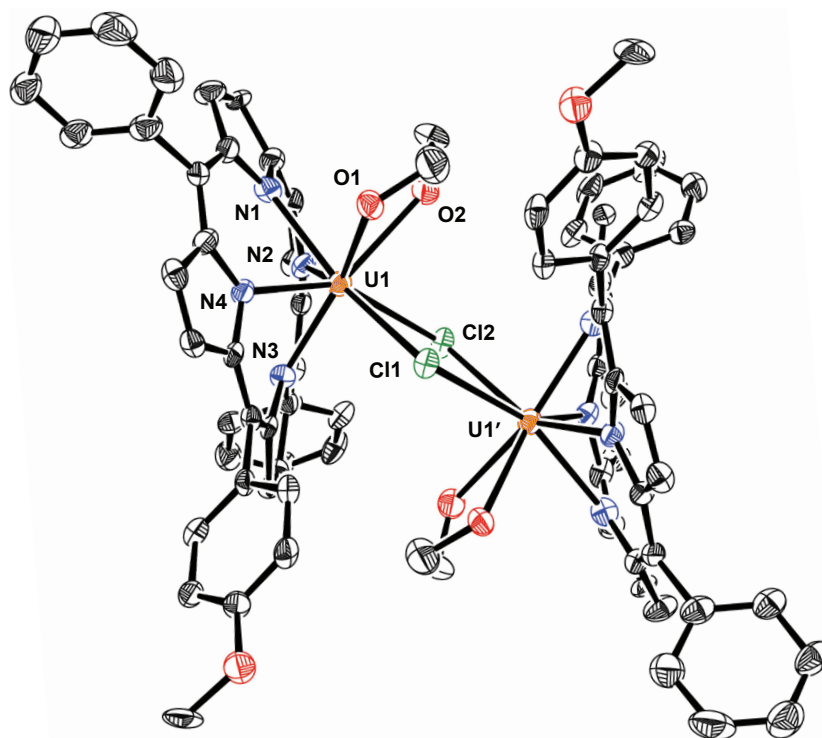


Figure 2.4. Molecular structure of uranium(IV) corrole **2.2**. Thermal ellipsoids are set to a 50% probability level. Hydrogen atoms, and both the mesityl and DME methyl groups, have been omitted for clarity.³⁹

Table 2.2. Crystal and Refinement Data for Complexes **2.1** and **2.2**

Complex	2.1	2.2
Formula	C ₉₆ H ₉₄ Cl ₂ N ₈ O ₆ Th ₂	C ₉₆ H ₉₄ Cl ₂ N ₈ O ₆ U ₂
Molecular weight	1990.77	2002.75
Space Group	C2/c	C2/c
<i>a</i> (Å)	26.5585(9)	27.0738(14)
<i>b</i> (Å)	23.3363(9)	23.6955(12)
<i>c</i> (Å)	20.8898(7)	20.6036(11)
<i>a</i> (°)	90	90
<i>b</i> (°)	123.790(2)	123.272(2)
<i>g</i> (°)	90	90
<i>V</i> (Å ³)	10760.0(7)	11051.0(10)
<i>Z</i>	4	4
ρ_{calcd} (g/cm ³)	1.229	1.204
<i>F</i> ₀₀₀	3952	3968
μ (mm ⁻¹)	2.858	3.021
Refl'ns collected	29024	37647
Indep. refl'ns	9629	10080
<i>R</i> _{int}	0.0660	0.0582
<i>R</i> ₁ , <i>wR</i> ₂	0.0474/0.1094	0.0527/0.1450
<i>R</i> ₁ , (all data)	0.0757	0.0833
GoF	0.980	1.038
Res. peak/hole (e ⁻ / Å ³)	3.230/-1.332	3.002/-1.016

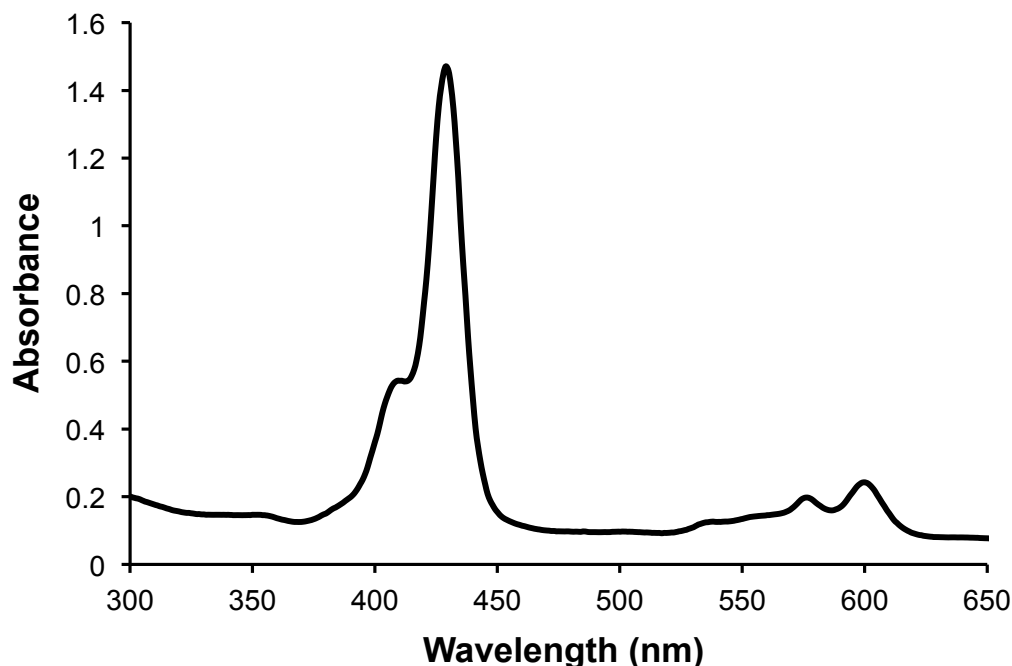


Figure 2.5. UV–visible absorption spectrum of **2.1** (1 μ M) in DCM.

UV-vis Spectroscopy. The two actinide corroles yield nearly identical UV–visible spectra (Figures 2.5 and 2.6, respectively), with each displaying a single Soret band (428 and 427 nm for **2.1** and **2.2**, respectively). This peak is markedly different from those observed for both the free-base and lithiated chromophores, and is indicative of a loss of planarity of the corrole. Similar spectra are observed for the Ga, Zr, Al and lanthanide corroles, which all possess significant ring distortion as a result of the metal center sitting significantly above the plane of the ligand.^{31,34,49,50} Additionally, both complexes show two broad Q bands, at 576 and 600 nm for **2.1**, and 575 and 602 nm for **2.2**, respectively, consistent with HOMO and LUMO transitions described by the Gouterman four-orbital model for corroles.⁵¹ At much higher concentrations (10 mM), a band is visible at 880 nm for the uranium complex (Figure 2.6, inlay). This feature is absent from the spectra of both the thorium and free base corroles, and may arise as a result of an increased allowedness of f – f transitions due to coupling across the chloride bridges. However, the large extinction coefficients of corroles, combined with the relatively low intensity of Laporte forbidden f – f transitions, prevent sufficient resolution for definitive assignment.

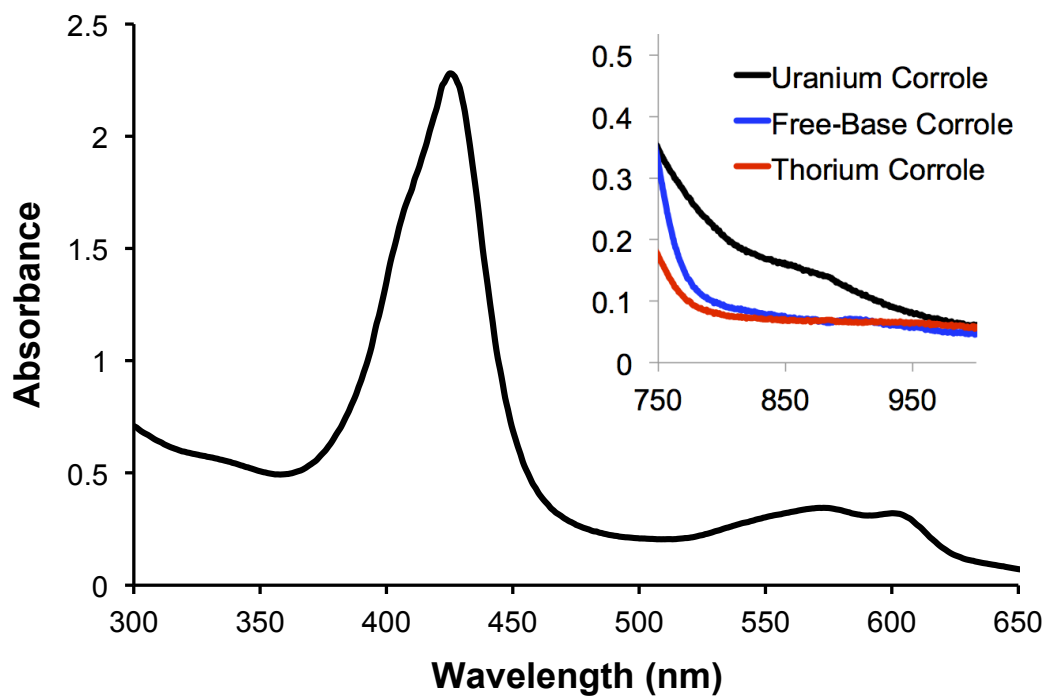
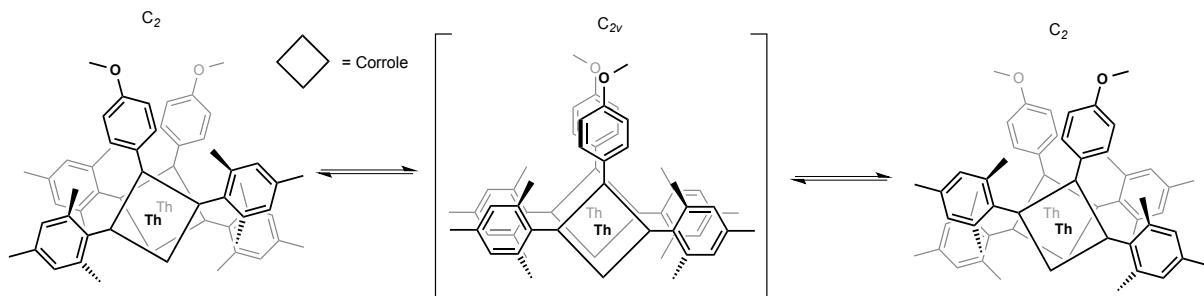


Figure 2.6. UV–visible absorption spectrum of **2.2** (1 μM) in DCM. Inlay: Overlay of the absorption spectra of **2.1**, **2.2** and the free base corrole (10 mM) in DCM.

Scheme 2.2. Pseudo-Rotation About the Th–Th Axis of **2.1**, Averaging to a C_{2v} Symmetry at Elevated Temperatures, but Locking into a C_2 Symmetry upon Cooling



NMR Spectroscopy. The ambient temperature ^1H NMR spectrum of **2.1** is straightforward in the aliphatic region. Four singlets can be assigned to the one *p*-methoxy, and three mesityl- CH_3 protons. Two additional broadened singlets correspond to the protons of the coordinated DME molecule, which is exchanging rapidly in CD_3CN . However, the resonances in the aromatic region are broadened at room temperature. Upon cooling to $-30\text{ }^\circ\text{C}$, the aromatic peaks can be resolved, but additional peaks are observed in the aliphatic region. The dynamic solution behavior seen in the aromatic region is similar to that observed for the analogous lanthanide corroles, and is attributed to the highly facile exchange of coordinating solvent.³⁴

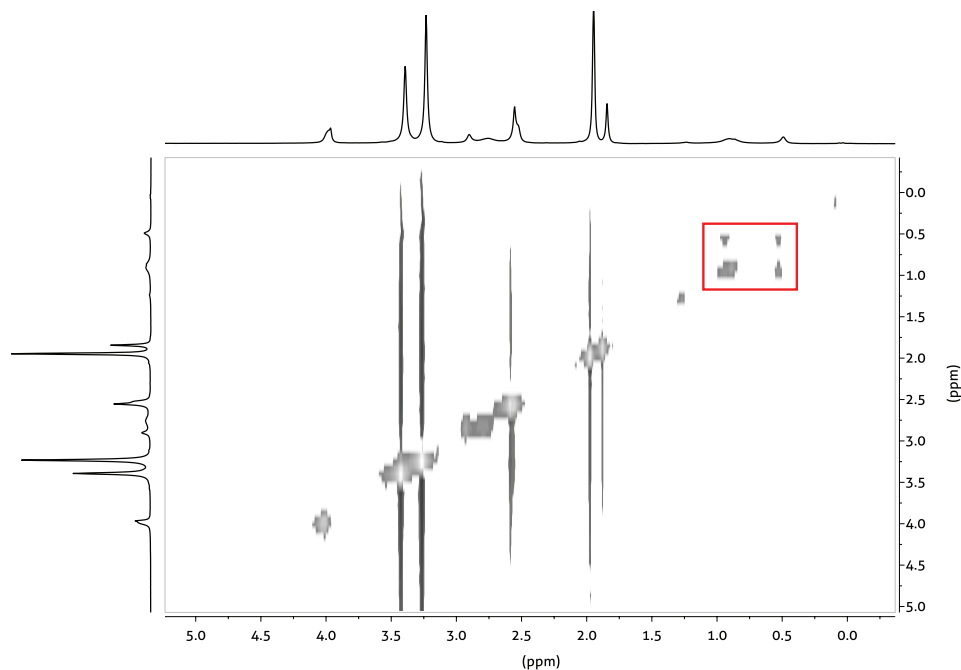


Figure 2.7. 2D ^1H – ^1H EXSY spectrum of **2.1** in CD_3CN at $-30\text{ }^\circ\text{C}$ and $T_m = 0.5\text{ s}$. Note: cross peaks are highlighted in red.

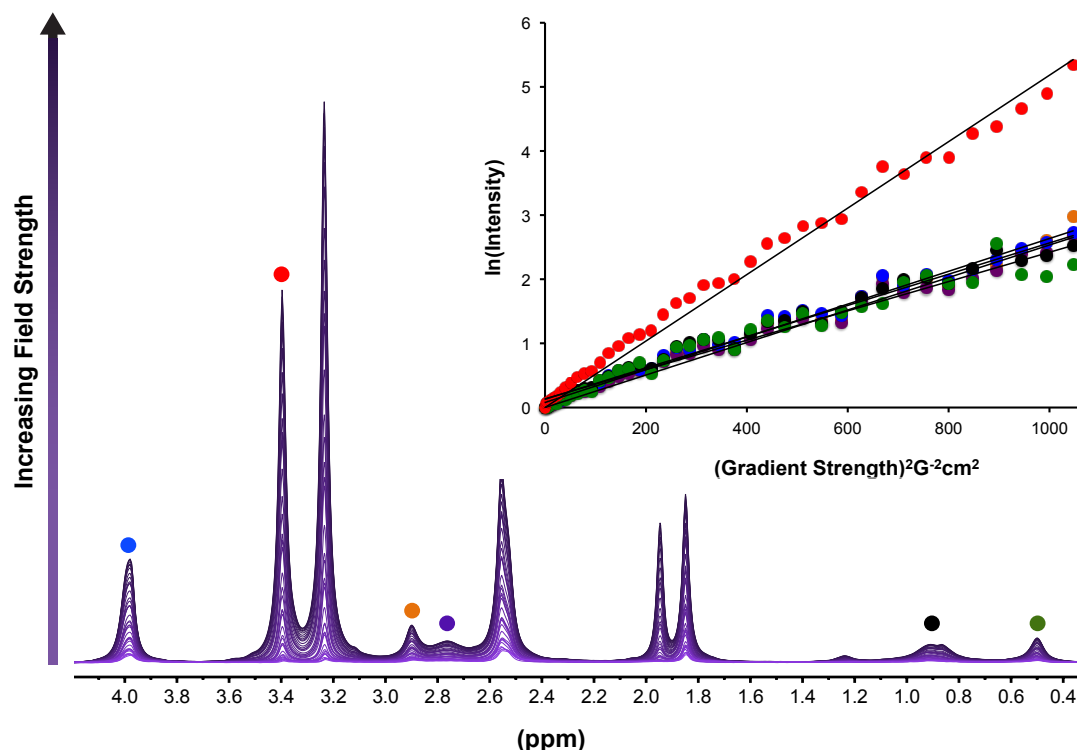


Figure 2.8. Stacked array of DOSY ^1H NMR spectra for **2.1** in CD_3CN at $-30\text{ }^\circ\text{C}$, measured with a linear increasing gradient strength. Inlay: Plot of the square of the gradient strength vs. the natural log of peak intensity.

However, the splitting of the aliphatic peaks is unique to the dimeric actinide corroles, and therefore could either be due to an equilibrium between the dimer observed in the solid state and a potential monomer in solution, or to an intrinsic pseudo-rotational mode of the dimer complex itself (Scheme 2.2).

Upon performing DOSY ^1H NMR spectroscopy, a single diffusion coefficient was observed ($2.55 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$), consistent with the presence of the dimeric species ($r_s = 9.9 \text{ \AA}$) (Figure 2.8). At low temperature, six singlets were observed for the mesityl- CH_3 protons, implying two inequivalent sets of mesityl groups, consistent with C_2 symmetry, and mirroring what is observed in the crystal structure. The EXSY ^1H NMR of **2.1** at $-30\text{ }^\circ\text{C}$ (Figure 2.7) exhibited cross peaks showing chemical exchange between the two sets of mesityl methyls, implying that the dynamic process was only slowed, and not averted, at this temperature. Upon warming, a rapid pseudo-rotation along the Th–Th axis leads to an averaging of the chemical environment that results in a C_{2v} symmetry whereby the six mesityl groups are equivalent (Scheme 2.2). This rotational process is further supported by the behavior of the *p*-methoxy group, which remains equivalent by virtue of a C_2 axis even in the staggered conformation, and is thus observed as a single peak across varying temperatures. The proton resonances for **2.2** are broad and paramagnetically shifted, as expected for a complex with an f^2 uranium(IV) center (*see below*).

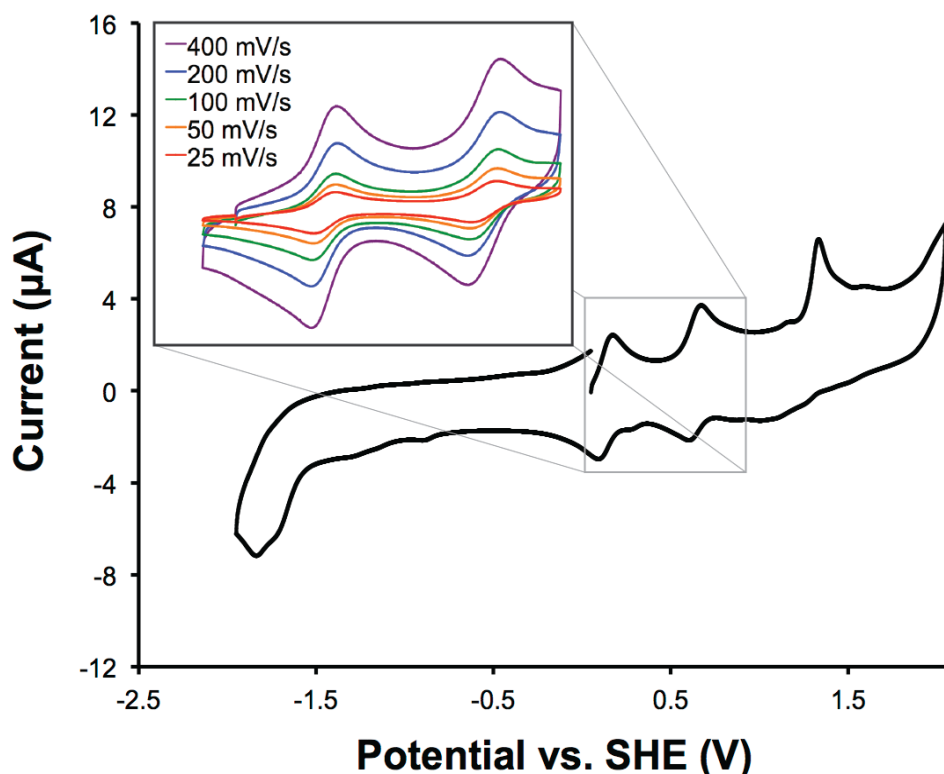


Figure 2.9. Cyclic voltammogram of **2.1** (1 mM) at 100 mV/s in MeCN, 25 °C. Inlay: Variable scan rate cyclic voltammograms of **2.1** for the highlighted redox waves.

Electrochemistry. Cyclic voltammetry (CV) experiments show that the thorium corrole undergoes two reversible processes ($E_{1/2} = 124$ and 616 mV; Figure 2.9). Additionally, there is an irreversible oxidation at 1.32 V and an irreversible reduction at -1.81 V. Thorium(IV) is not expected to display any redox behavior within the potential range discussed here.⁵² Therefore, these features may confidently be regarded as ligand-based processes, arising from changes in the macrocycle electronic structure due to both the electron-withdrawing effect of the metal center, and the extreme distortion of the corrole ring from planarity upon binding to the actinide. This effect has been observed for a variety of non-redox active metals upon corrole chelation, where generally, the redox potential of the metallocorrole correlates well with the electronegativity of the bound ion, as with the P, Al, Ge, Ga and Sn examples.^{49,50,53,54} However, outliers to this trend occur, where Bi, despite being the most electronegative of the aforementioned series, displays the lowest oxidation potential.⁴⁶ This electrochemical behavior can be reasonably explained when considering the greater distortion from planarity—and thus aromaticity—seen upon complexation, and illustrates the synergy of these two effects.

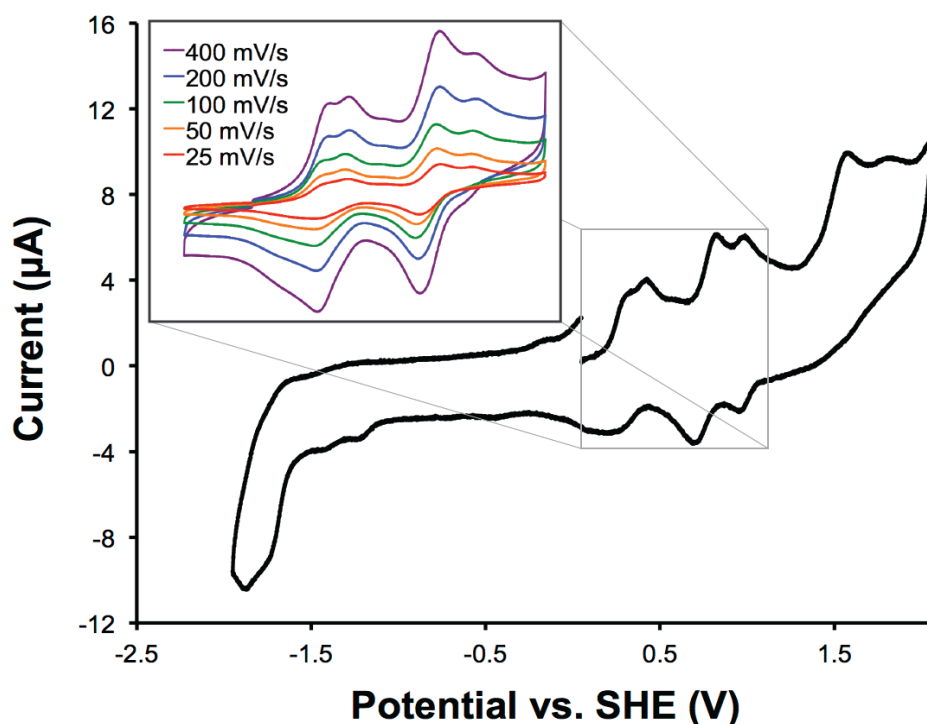


Figure 2.10. Cyclic voltammogram of **2.2** (1 mM) at 100 mV/s in MeCN, 25 °C. Inset: Variable scan rate cyclic voltammograms of **2.2** for the highlighted redox waves.

The CV for **2.2** is more complex (Figure 2.10). The first two oxidations, which were reversible in complex **2.1**, are only quasireversible ($E_{1/2} = 124$ and 616 mV) and have additional oxidative shoulders ($E_{pa} = 0.44$ and 1.05 V). The potential of these shoulders remains constant as a function of scan rate (Figure 2.10, inlay), eliminating the possibility of an electrochemical-chemical-electrochemical (ECE) mechanism. Additionally, these peaks are absent in the thorium case, indicating that this redox behavior may arise due to electronic communication between the uranium centers, consistent with the low-intensity transition observed in the UV-visible spectrum. However, current literature suggests that the electronic structure of these compounds is quite complex, and the exact nature is forthcoming for these actinide examples at this time.^{55,56} The oxidations are positively shifted for **2.2** when compared to **2.1** (Figure 2.11), reflecting the larger electronegativity of uranium, as well as the greater distortion of the corrole ring. Additionally, an irreversible oxidation at 1.54 V and a reduction at -1.85 V mirror those seen in the thorium case. The similarity in redox properties between the U(IV) and Th(IV) corroles has also been noted between the actinide porphyrins and is attributed to the ligand centered nature of the redox processes.⁵⁷

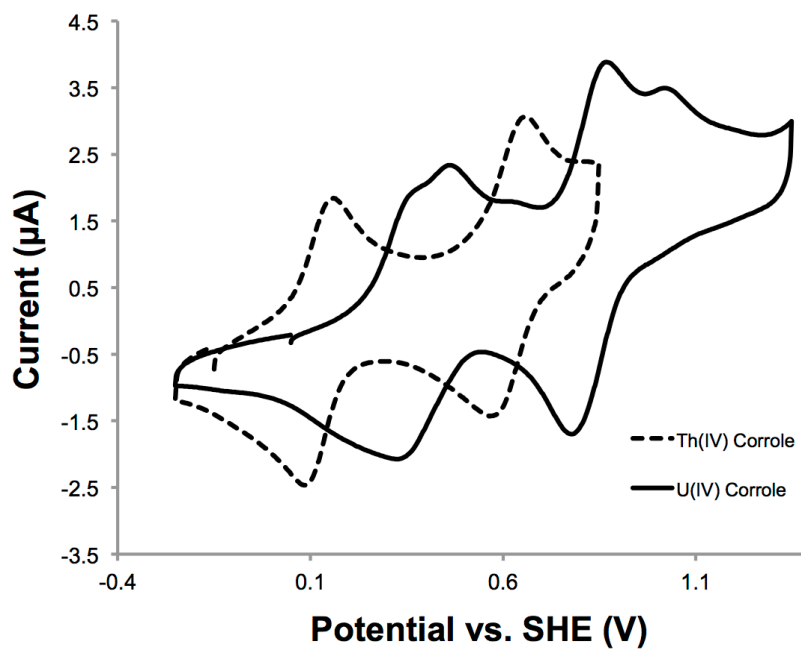


Figure 2.11. Overlay of cyclic voltammograms of **2.1** and **2.2** (1 mM) at 100 mV/s in MeCN, 25 °C.

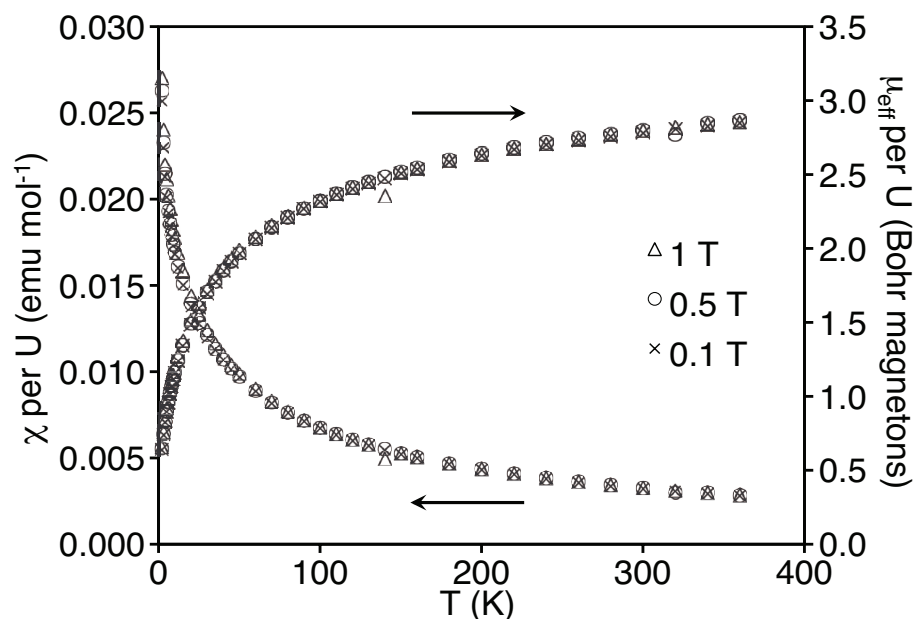


Figure 2.12. Variable temperature magnetic susceptibility of **2.2**.

Magnetic Susceptibility. The variable temperature magnetic moments measured for **2.2** are in good agreement with those predicted for U(IV) with a 3H_4 ground-state. Upon cooling, the magnetic moment trends towards zero (Figure 2.12), consistent with an orbital singlet ground-state ($m_j = 0$), and similar to that observed for related uranium complexes.⁵⁸ Likewise, the magnetic moment of **2.2** at 360 K ($2.85 \mu_B$) is within the range observed for U(IV) amide complexes ($2.44 \mu_B$ to $3.48 \mu_B$)^{59,60} and similar to that of U(phthalocyanine)₂ (*ca.* $3.1 \mu_B$).⁶¹ Taken together, this leads to the assignment of both metal centers as U(IV).

Conclusions

To summarize, the first examples of actinide corroles have been prepared in a facile and high-yielding manner and characterized. Characterization by X-ray crystallography revealed both molecules to be bis(μ -chlorido) dimers with significant distortion of the metal centers from the N_4 plane of the corrole ligand. The diamagnetic thorium complex **2.1** was well suited for NMR studies which revealed that the dimer has an intrinsic pseudorotational mode about the Th–Th axis in solution. Cyclic voltammetry of complexes **2.1** and **2.2** showed several accessible oxidations as well as a reduction that are likely ligand centered with potentials dependent on both the metal center and corrole ring distortion. These actinide corrole complexes represent a new class of macrocyclic complexes in an area that is underdeveloped for this group of elements. We believe these compounds have the potential to provide a robust platform for elucidating actinide bonding and reactivity and proposals for such chemistry are presented in the Future Directions chapter.

Experimental Section

General procedures. Unless otherwise noted, all reactions were performed using standard Schlenk line techniques or in an MBraun N₂-atmosphere glovebox (< 1 ppm O₂/H₂O). All glassware and Celite were stored in an oven at ~ 150 °C. Dimethoxyethane (DME), acetonitrile (MeCN), tetrahydrofuran (THF), hexane and dichloromethane (DCM) were dried and degassed using a Phoenix Solvent Drying System commercially available from JC Meyer Solvent Systems. CD₃CN was vacuum-transferred from CaH₂ and degassed with three freeze-pump-thaw cycles. All NMR spectra were recorded at the specified temperature on Bruker DRX 500 and AV-600 spectrometers. Temperature calibration was performed using changes in chemical shift separation of ethylene glycol at high temperature, and methanol at low temperature. ¹H chemical shifts (δ) were calibrated using residual solvent peaks. UV–visible spectra were determined with a Varian Cary 50 UV–vis spectrophotometer, using a Schlenk-adapted 1 mm quartz cell. Mass spectral data (ESI-MS, positive mode) were obtained at the University of California, Berkeley Microanalytical Facility, using vacuum-dried samples dissolved in THF. Melting points were determined on an Optmelt SRS using sealed capillaries prepared under nitrogen and are uncorrected. Mes₂(*p*-OMePh)corroleLi₃•6THF,³¹ ThCl₄(DME)₂³² and UCl₄³³ were prepared according to literature procedures.

Thorium (IV) 5,15-bis(2,4,6-trimethylphenyl)-10-(4-methoxyphenyl)corrole bis-dimethoxyethane (2.1). A solution of Mes₂(*p*-OMePh)corroleLi₃•6THF (100 mg, 0.091 mmol) in 2 mL DME was added to a suspension of ThCl₄(DME)₂ (51 mg, 0.092 mmol) in 2 mL DME to produce a dark red solution. The reaction mixture was stirred for 1 d, after which time a purple solid had precipitated. The reaction mixture was filtered and the solid was extracted with DCM (2 × 3 mL), filtered through Celite, concentrated until saturation, and carefully layered with hexanes to afford the product as dark red needles (85 mg, 93% yield). Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a solution of **2.1** in DCM at -40 °C. ¹H NMR (500 MHz, CD₃CN, room temperature. Note: some peaks are broadened or partially coalesced at this temperature. Any assignments were confirmed by spectra taken at additional temperatures): δ 8.07 (s, br, Ar-*H*), 7.32 (s, br, Ar-*H*), 4.04 (s, 3H, C₆H₄OCH₃), 3.41 (s, 8H, (CH₂)₂O₂(CH₃)₂), 3.25 (s, 12H, (CH₂)₂O₂(CH₃)₂), 2.86 (s, 6H, C₆H₂CH₃), 2.59 (s, 6H, C₆H₂CH₃), 0.91 (s, 6H, C₆H₂CH₃). ¹H NMR (500 MHz, CD₃CN, -40 °C): δ 8.48 (s, Ar-*H*), 8.44 (s, Ar-*H*), 8.05 (s, Ar-*H*), 7.98 (d, *J* = 10 Hz, Ar-*H*), 7.92 (s, Ar-*H*), 7.72 (s, Ar-*H*), 7.53 (s, Ar-*H*), 7.41 (s, Ar-*H*), 7.30 (s, Ar-*H*), 7.22 (d, *J* = 5 Hz, Ar-*H*), 7.11 (s, Ar-*H*), 6.95 (s, Ar-*H*), 3.96 (s, br), 3.30 (s, br), 3.16 (s, br), 2.92 (s, br), 2.55 (s, br), 2.52 (s, br), 1.84 (s, br), 0.92 (s, br), 0.47 (s, br). UV–vis (nm): 428, 576, 600. ESI-MS (+) Calcd: 994.3712 for C₄₈H₄₇O₃N₄Cl₁Th₁ Observed: 994.3716. Mp: dec. > 270.2 °C

Uranium (IV) 5,15-bis(2,4,6-trimethylphenyl)-10-(4-methoxyphenyl)corrole bis-dimethoxyethane (2.2). A solution of Mes₂(*p*-OMePh)corroleLi₃•6THF (100 mg, 0.091 mmol) in 2 mL DME was added to a suspension of UCl₄ (35 mg, 0.092 mmol) in 2 mL DME to produce a dark red solution. The reaction mixture was stirred for 1 d. The solvent was removed in vacuo to yield a dark purple solid. The solid was extracted with DCM (2 × 3 mL), filtered through Celite, concentrated until saturation, and carefully layered with hexanes to afford the product as dark pink needles (76 mg, 83% yield). Single crystals suitable for X-ray

diffraction were obtained by slow diffusion of hexane into a solution of **2.2** in DCM at $-40\text{ }^{\circ}\text{C}$. ^1H NMR (500 MHz, CD_3CN , room temperature): δ 10.76 (s, br), 10.28 (s, br), 8.97 (s, br), 8.44 (s, br), 8.37 (s, br), 8.21 (s, br), 8.04 (d, $J = 5\text{ Hz}$), 7.49 (s, br), 7.36 (d, $J = 10\text{ Hz}$), 7.34 (s, br), 6.66 (s, br), 6.28 (s, br), 5.51 (s, br), 4.13 (s, br), 2.80 (s, br), 2.60 (s, br), 2.35 (s, br), 2.10 (s, br), 3.75–2.00 (s, br, under reported singlets), 1.90 (s, br), 1.30 (s, br), -8.28 (s, br). ^1H NMR (500 MHz, CD_3CN , $-40\text{ }^{\circ}\text{C}$): δ 13.20 (s, br), 10.31 (s, br), 9.21 (s, br), 8.63 (s, br), 8.34 (s, br), 7.57 (s, br), 7.35 (s, br), 7.30 (s, br), 5.59 (s, br), 5.55 (s, br), 4.43 (s, br), 3.39 (s, br), 3.30 (s, br), 3.18 (s, br), 2.56 (s, br), 2.20 (s, br), 1.81 (s, br), 1.24 (s, br), 0.87 (s, br), -1.16 (s, br), -3.24 (s, br), -13.94 (s, br). UV-vis (nm): 427, 575, 602. ESI-MS (+) Calcd: 1000.3839 for $\text{C}_{48}\text{H}_{47}\text{O}_3\text{N}_4\text{Cl}_1\text{U}_1$ Observed: 1000.3849. Mp: dec. $> 230.4\text{ }^{\circ}\text{C}$. $\mu_{\text{eff}} = 2.85\text{ }\mu_{\text{B}}$

Crystallographic procedures. X-ray structural determinations were performed at CHEXRAY, University of California, Berkeley, on a Bruker APEX II Quazar diffractometer. The instrument is Kappa Geometry with DX, and is a 3-circle diffractometer that couples a CCD detector⁶² with a sealed-tube source of monochromatized Mo $\text{K}\alpha$ radiation. A crystal of appropriate size was coated in Paratone-N oil and mounted on a Kaptan loop. The loop was transferred to the diffractometer, centered in the beam, and cooled by a nitrogen flow low-temperature apparatus that had been previously calibrated by a thermocouple placed at the same position as the crystal. Preliminary orientation matrices and cell constants were determined by collection of 60 10 s frames, followed by spot integration and least-squares refinement. The reported cell dimensions were calculated from all reflections with $I > 10\sigma$. The data were corrected for Lorentz and polarization effects; no correction for crystal decay was applied. An empirical absorption correction based on comparison of redundant and equivalent reflections was applied using SADABS.⁶³ All software used for diffraction data processing and crystal-structure solution and refinement are contained in the APEX2 program suite (Bruker AXS, Madison, WI).⁶⁴ Thermal parameters for all non-hydrogen atoms were refined anisotropically. For all structures, $R1 = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$; $wR2 = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{1/2}$, ORTEP diagrams were created using the ORTEP-3 software package and POV-ray.^{65,66}

DOSY NMR procedure. ^1H NMR spectra were recorded on a Bruker AV-600 spectrometer. DOSY spectra were recorded using Bruker's "ledbpgp2s" program with a diffusion delay (D) of 0.08 s and gradient length (δ) of $1300\text{ }\mu\text{s}$ for each sample. T_1 , and the 90° pulse width, were independently measured prior to running the DOSY experiment, and the spectra were recorded with a delay of 10 s ($4\times$ greater than T_1) in order to allow for adequate magnetic relaxation. The gradient strength was varied from 5% to 95%. The data were processed using MestrReNova software package (version 8.1.1).

The hydrodynamic radius of **2.1** was calculated using the Stokes-Einstein equation:

$$r_s = \frac{kT}{6\pi\eta D}$$

where k is the Boltzman constant, T is the temperature, η is the viscosity of the liquid, D is the diffusion constant and r_s is the hydrodynamic radius of the molecule.

Electrochemical procedures. Solution cyclic voltammograms were recorded with a Gamry Reference 600TM potentiostat, using a glassy carbon working electrode (0.07 cm²), a platinum counter electrode and a floating silver reference electrode. Ferrocene ($E_{Fc}^{+/0} = 0.64$ V vs. SHE) was added at the end of each electrochemical experiment as an internal reference. Acetonitrile was used as the solvent with 0.1 M (ⁿBu₄N)(PF₆) as the supporting electrolyte. All examinations of solutions by CV were conducted in an MBraun N₂-atmosphere glovebox (< 1 ppm O₂/H₂O).

Magnetism procedures. Uranium corrole **2.2** (16.4 mg) was sandwiched between two plugs of quartz wool (Hereaus, 9.9 mg) in a 4 mm OD quartz tube, which was flame sealed on both ends. Sample magnetization was recorded at 0.1 T, 0.5 T, and 1 T using a Quantum Designs MPMS SQUID magnetometer. Magnetization was corrected for the diamagnetism of the quartz wool using Pascal's constants (no correction for the diamagnetism of the quartz tube is needed as the quartz tube never leaves the SQUID coils). Molar susceptibility was corrected for the presence of a small amount of ferromagnetic impurity (M_{ferro}), the diamagnetism of the quartz wool (χ_{QW}), ligands and uranium (χ_{dia}) using Pascal's constants, and calculated using the following equation:

$$\chi_{mol} = \frac{(\text{molecular weight})}{(\text{sample mass})} \left[\frac{(M_{meas} - M_{ferro})}{H} - \chi_{QW} \right] - \chi_{dia}$$

where χ_{mol} is the molar susceptibility, M_{meas} is the measured magnetization, M_{ferro} is the magnetization of the ferromagnetic impurity, which is temperature independent and assumed to be identical at all fields, χ_{QW} is the contribution to the susceptibility due to the quartz wool, χ_{dia} is the diamagnetic correction, and H is the applied field.

Correction for paramagnetic impurity: Two ferromagnetic impurities are commonly encountered in laboratory samples, steel or iron metal and magnetite or other ferrites from oxide coating on stainless steel lab equipment. Of these, magnetite is far more likely to be encountered. In general, the magnetization of ferromagnets is temperature independent below the Curie temperature, which is 1040 K and 860 K for iron and magnetite, respectively, so magnetization of the impurity is temperature independent for this experiment. The magnetization of ferromagnets is also largely field-independent above the anisotropy field, which is 0.6-1.5 T and 0.2 T for steel/iron, and magnetite, respectively. Below the anisotropy field, the magnetization of a magnet is roughly linear with applied field. Based on the assumption that the impurity is magnetite or some other ferrite resulting from the abrasion of stainless steel lab equipment, the data were corrected for a temperature and field independent ferromagnetic impurity. M_{ferro} was allowed to vary to minimize least squares difference between χ_{mol} at different fields, which produced a saturation magnetization of $M_{ferro} = 1.52 \times 10^{-5}$ emu.

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Chapter 2

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Chapter 3

Synthesis, Characterization and Dioxygen Reactivity of a Series of First Row Transition Metal Tris(2-pyridylmethyl)amine Complexes

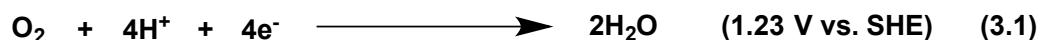
Chapter 3

Overview

The neutral tripodal N-donor ligand tris(2-pyridylmethyl)amine (TPA) has been utilized to support a wide variety of transition metal complexes. Particular attention has been given to iron and copper TPA derivatives as biomimetic systems for oxygen activation. The following chapter describes the synthesis and characterization of a series of first row transition metal TPA complexes intended for the systematic study of the range of molecular properties that arise as a result of metal center variation, and the effect these characteristics have on oxygen activation. Portions of this chapter have previously been published in: Ward, A. L., Elbaz, L., Kerr, J. B., and Arnold, J. "Nonprecious Metal Catalysts for Fuel Cell Applications: Electrochemical Dioxygen Activation by a Series of First Row Transition Metal Tris(2-pyridylmethyl)amine Complexes." *Inorg. Chem.* **2012**, 51, 4694.

Introduction

Determining the factors that govern the activation of dioxygen by transition metal coordination compounds is of fundamental importance to a wide variety of synthetic and biological transformations.¹⁻¹⁰ One such reaction is the selective reduction of oxygen to water, which is a vital in the energy transfer processes of aerobic organisms,¹¹ but also has particular relevance to fuel cell technologies (Equation 3.1).¹² Recently, the use of first row transition



metal coordination compounds as oxygen reduction catalyst alternatives to solid-state platinum based materials has gained attention.¹³⁻¹⁶ The implementation of a molecular approach is contingent upon (i) the design of simple systems capable of selective and efficient oxygen reduction, (ii) a thorough and detailed understanding of the molecular properties as a reference for extrapolating to hybrid materials and (iii) the ability to tune the system for desired reactivity and compatibility in fuel cell applications.

The devising of such molecular systems has taken a biomimetic approach, seeking to model the active sites of oxygen binding and activating enzymes, such as the P450 family of proteins and blue-copper laccases (Figure 3.1).^{4,17-19} As such, great attention has been given to complexes that contain iron and copper, the two transition metal ions most often utilized in nature for manipulating oxygen. However, oxygen activation and binding have been demonstrated with all of the late first row transition metals, employing a diverse set of ligand systems. The oxygenation chemistry of both iron and cobalt has been heavily focused on porphyrins^{4,17,20} and corroles,¹⁸ where catalytic reduction has been observed. Additionally, a propensity for four-electron reduction has been recently demonstrated with both a monomeric manganese complex,²¹ as well as a nickel bis(diphosphine) complex.²² The study of copper O₂ activation chemistry has been tailored to emulate copper laccases, often utilizing tris(2-pyridylmethyl)amine (TPA; also abbreviated TMPA or Npy3) analogues (Figure 3.2a) as molecular mimics.^{10,12,19,23,24} Clearly, many first row coordination compounds exhibit a propensity for oxygen activation and reduction; however, given the diversity in coordination environments, extracting a coherent design strategy with regard to the metal center remains difficult.

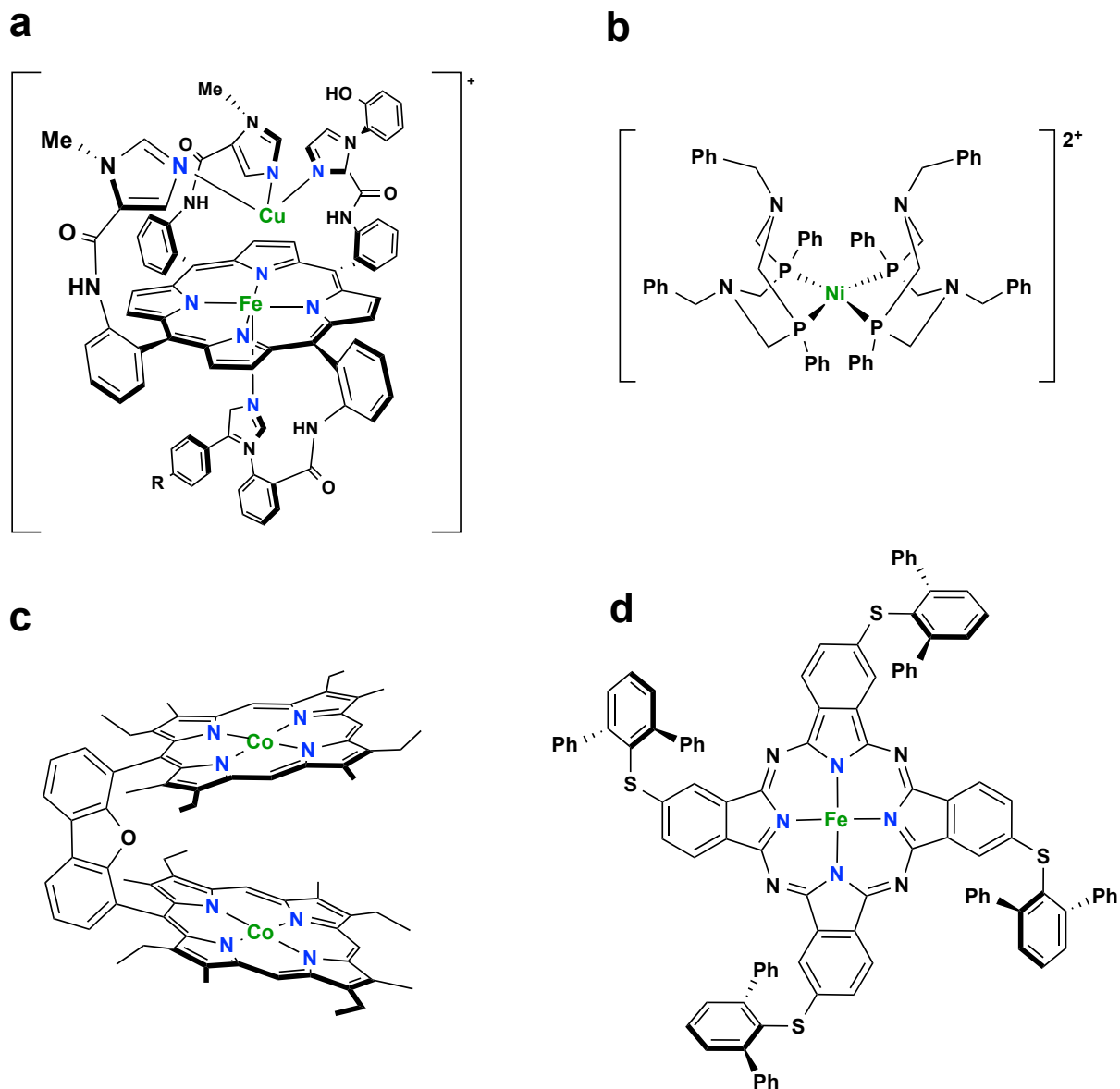


Figure 3.1. Molecular oxygen reduction catalysts. a) Synthetic mimic of cytochrome *c* oxidase.⁴ b) Nickel bis(diphosphine) complex.²² c) Cobalt "Pacman" porphyrin complex.¹⁷ d) Iron phthalocyanine complex.¹⁴ Note: the variety of first row transition metals used are highlighted in green, and the nitrogen donor motif often employed in both natural and synthetic oxygen reduction systems is highlighted in blue.

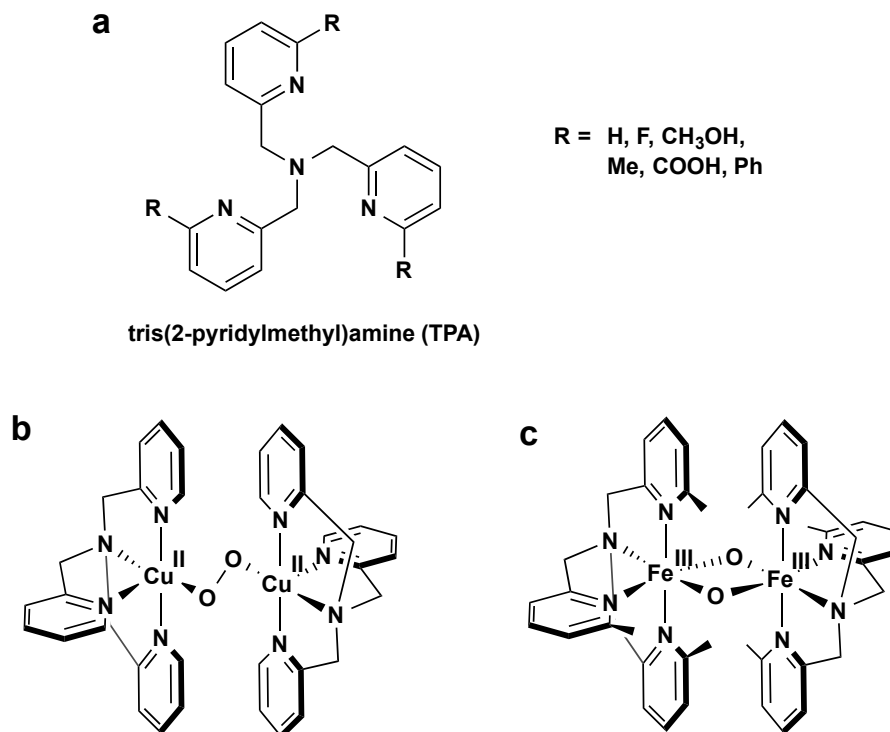


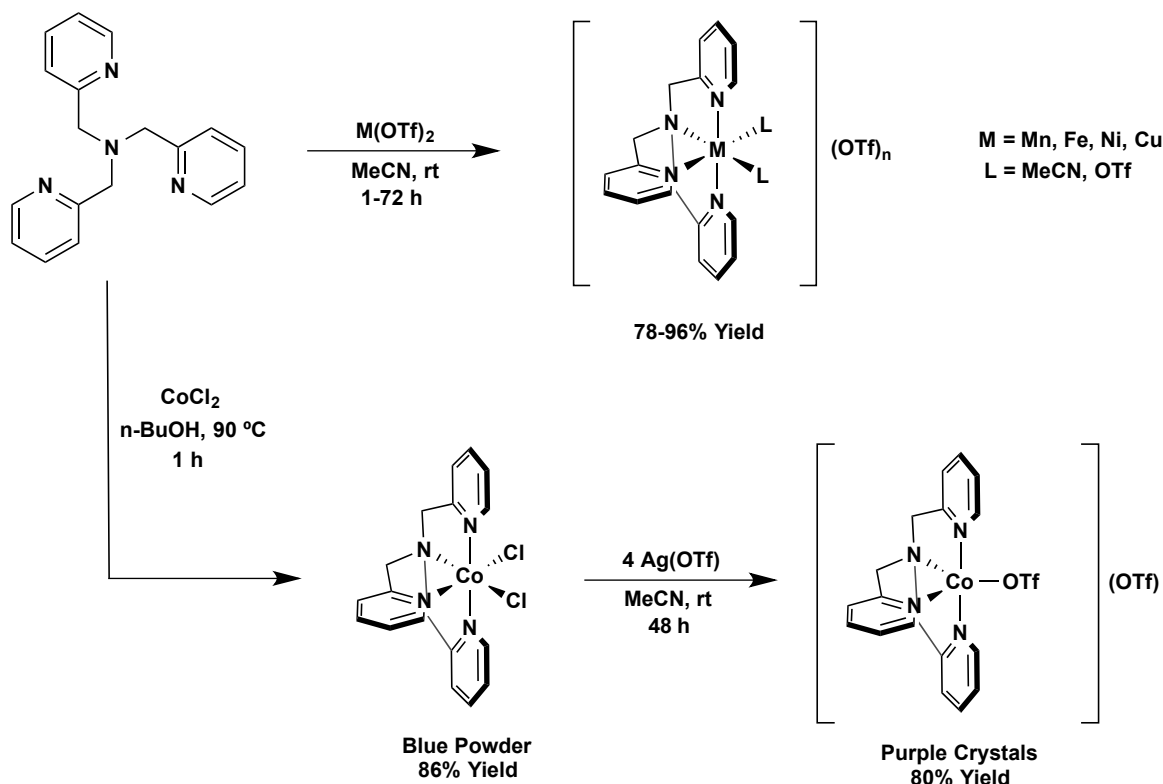
Figure 3.2. Ligand of interest TPA and significant O_2 adducts. a) Tris(2-pyridylmethyl)amine (TPA) ligand and various derivatives.³¹⁻³⁶ b) $[\text{Cu}_2(\mu\text{-O}_2)(\text{TPA})_2](\text{PF}_6)_2$.³⁰ c) $[\text{Fe}_2(\mu\text{-O})_2(5\text{-Me-TPA})_2](\text{ClO}_4)_2$.³⁶

Copper and iron derivatives of TPA (Figure 3.2b and 3.2c) have been studied as O_2 activation catalysts for some time.^{10,19,31-34} However, the dioxygen reactivity of other late transition metal complexes of this ligand has not been reported. Given our interest in determining the best method for selecting a molecular species to employ as a fuel cell catalyst, we sought to synthesize a series of TPA transition metal complexes in order to study the effect of varying the metal center in a ligand system known to be capable of oxygen reduction. Divalent manganese, iron, cobalt, nickel and copper bis(triflate) TPA homologues were prepared for this purpose; their detailed solution and solid-state characterization and reactivity towards dioxygen is described.

Results and Discussion

The advantages of homogeneous catalysis over heterogeneous catalysis are that the catalytic species of interest, as well as reactive intermediates, are readily characterized via classical methods.^{35,36} In turn, this allows for straightforward deciphering of the catalytic mechanism and subsequent catalyst tuning. The aim of this work is to utilize a molecular catalyst in a traditionally heterogeneous system. This will provide a means for relating molecular behavior to performance seen in the applied system by first accurately and thoroughly characterizing the molecular species of interest.

Scheme 3.1. Synthesis of TPA Complexes **3.1–3.5** (Top: Synthesis of Complexes **3.1**, **3.2**, **3.4** and **3.5** Achieved via Combination of the Corresponding M^{2+} Salt and the TPA Ligand Bottom: Synthesis of Complex **3.3** via Salt Metathesis with the Co(TPA)Cl_2 Complex)



Synthesis and Structural Properties. As an initial proof of concept, a simple molecular system capable of ORR and compatible with a fuel cell environment was selected for study. The TPA scaffold has been shown to support complexes capable of oxygen activation.^{19,23,31,33,37} Triflate anions (OTf) are weakly coordinating, providing the possibility for open coordination sites, and closely resemble the terminal perfluoroalkylsulfonate anions present in the Nafion polymer electrolyte membrane.^{38,39} Given their compatibility with our design criteria, divalent manganese, iron, nickel and copper bis(triflate) complexes of TPA were synthesized by reaction of the corresponding M^{2+} triflate salt with the ligand in acetonitrile (Scheme 3.1, top). The cobalt(II) derivative was synthesized via salt metathesis between Co(TPA)Cl_2 ⁴⁰ and Ag(OTf) (Scheme 3.1, bottom). Filtration of the reaction mixtures followed by recrystallization from MeCN afforded the desired $(\text{TPA})\text{Mn}(\text{OTf})_2$ (**3.1**), $[(\text{TPA})\text{Fe}(\text{MeCN})_2](\text{OTf})_2$ (**3.2**), $[(\text{TPA})\text{Co}(\text{OTf})](\text{OTf})$ (**3.3**), $[(\text{TPA})\text{Ni}(\text{MeCN})_2](\text{OTf})_2$ (**3.4**) and $[(\text{TPA})\text{Cu}(\text{MeCN})](\text{OTf})_2 \cdot (\text{MeCN})$ (**3.5**) in good to excellent yields (78-96%).

$(\text{TPA})\text{Mn}(\text{OTf})_2$ is unusual in that most Mn(TPA) complexes found in the literature are bimetallic catalase mimics,^{42,43} while **3.1** (Figure 3.3) is monomeric. The relatedness of oxygenase chemistry to oxygen reduction, as well as recent literature precedent for oxygen reduction by a monometallic Mn complex containing nitrogen donors,²¹ lend support to utilizing **3.1** as an

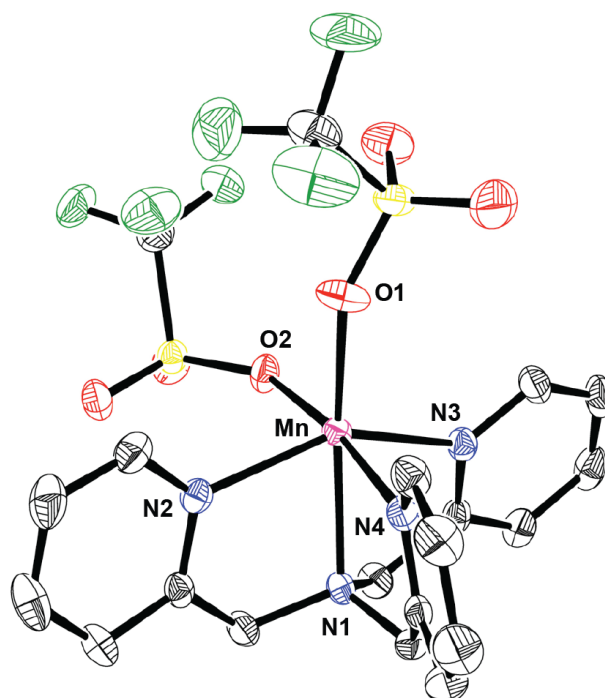


Figure 3.3. Molecular structure of manganese complex **3.2**. Thermal ellipsoids are set to a 50% probability level and hydrogen atoms have been omitted for clarity.

ORR catalyst. As with all the complexes in the M^{2+} triflate series **3.1–3.5** in the solid-state, the TPA ligand is coordinated in a tripodal tetradentate fashion in **3.1**. The geometry about the manganese center in **3.1** is a distorted octahedron, with two triflate anions occupying the remaining coordination sites, and represents the only neutral complex in **3.1–3.5**. The TPA ligand is folded away from the steric and electronic bulk of the coordinated triflate ions, as evidenced by the average $N_{\text{pyridine}}-\text{Mn}-N_{\text{amine}}$ angle deviation from the mean square plane of the octahedron of $14.22(6)^\circ$.

The $\text{Mn}-N_{\text{amine}}$ distance (Table 3.1) of $2.289(2)$ Å is similar to that of the closely related manganese(II) TPA dichloride,⁴⁴ which is also a neutral octahedral complex. The three pyridyl nitrogens are bound to the manganese center at similar distances, $2.235(2)$, $2.243(2)$ and $2.252(1)$ Å respectively, with the nitrogen trans to the triflate ligand having the longest bond length as expected due to the higher trans effect of the anionic triflate. The triflate distances concur with this assessment, with one anion being labile, allowing for an available coordination site for catalysis. The triflate trans to the pyridyl nitrogen has a longer distance ($2.169(1)$ Å) than that of the triflate trans to the amine ($2.114(1)$ Å), which lacks a π system capable of an additional π trans effect.

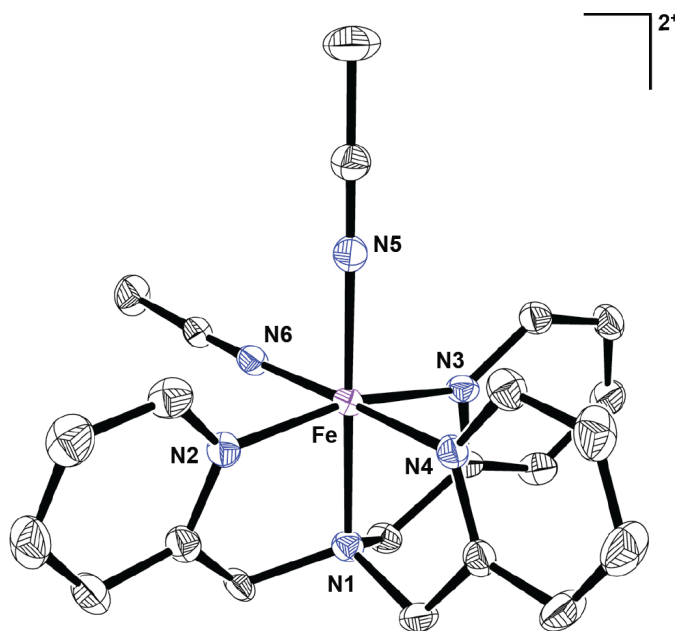


Figure 3.4. Molecular structure of iron complex **3.2**. Thermal ellipsoids are set to a 50% probability level and hydrogen atoms and outer sphere anions have been omitted for clarity.

Iron(II) TPA derivatives have been studied extensively as bio-inspired non-heme catalysts for oxygen activation and transfer reactions.^{34,45} The iron derivative **3.2** (Figure 3.4) is dicationic and adopts an octahedral coordination mode, similar to other iron oxygen activation catalysts. In addition to the η_4 -TPA, two acetonitrile molecules are bound to the Fe(II) center in **3.2** and two triflate anions are present in the secondary coordination sphere.

The Fe–N_{amine} distance (1.978(3) Å) is the longest of the nitrogens bound to the metal center, as is expected given its lack of ability for π donation. The Fe–N_{pyridine} bonds are quite similar (1.962(3), 1.959(3) and 1.953(3) Å respectively) with the nitrogen trans to the coordinated acetonitrile having the shortest distance, presumably due to trans effects. While labile enough to allow for substrate binding, the acetonitrile distances represent the shortest for the iron derivative, and are likely a consequence of the favorability of enforcing a low-spin state. Consistent with other iron TPA complexes, the stronger field acetonitrile ligands bound in **3.2** allow for a low-spin 18-electron complex, whereas neutral derivatives with anions directly bound to the iron center yield high-spin complexes.

Chapter 3

Table 3.1. Selected Bond Lengths (Å) and Angles (°) for Complexes **3.1**–**3.5**

Complex	3.1	3.2 ^a	3.3	3.4	3.5 ^b
Bond Lengths (Å)					
M–N1	2.289(2)	1.978(3)	2.162(5)	2.090(2)	2.007(7)
M–N2	2.235(2)	1.962(3)	2.037(5)	2.071(2)	2.037(3)
M–N3	2.243(2)	1.959(3)	2.039(5)	2.069(2)	-
M–N4	2.252(1)	1.953(3)	2.041(5)	2.071(2)	-
M–N5	-	1.933(3)	-	2.034(2)	1.949(7)
M–N6	-	1.947(3)	-	2.126(2)	-
M–O1	2.114(1)	-	2.016(4)	-	-
M–O2	2.169(1)	-	-	-	-
Bond Angles (°)					
N1–M–N2	76.13(6)	83.6(1)	79.7(2)	81.49(7)	82.7(2)
N1–M–N3	74.19(6)	83.2(1)	79.0(2)	80.96(7)	-
N1–M–N4	77.01(6)	85.7(1)	79.0(2)	82.96(7)	-
N2–M–N4	81.31(6)	91.6(1)	118.2(2)	88.58(7)	120.0
N1–M–N5	-	178.6(1)	-	178.03(7)	180.0
N1–M–O1	166.52(6)	-	175.5(2)	-	-

^aSelect bond lengths (Å) and angles (°) for **3.2** are appended from ref. 48. ^bComplex **3.5** possesses a unit cell comprised of three highly symmetric 1/3 fragments of the molecule. Each possesses a C_3 element of symmetry that generates the rest of the molecule. As a result, the M–N1, M–N2 and M–N5 distances, and N1–M–N2 angle, are presented as an average of the three.

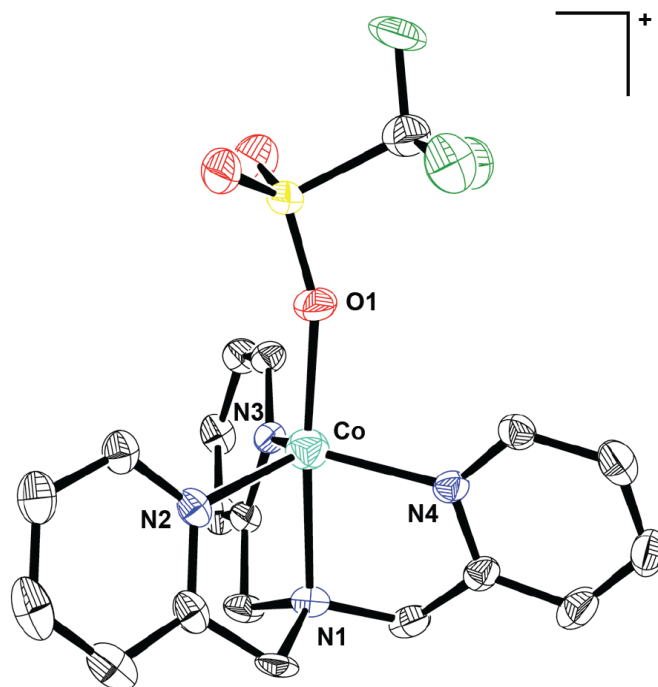


Figure 3.5. Molecular structure of cobalt complex **3.3**. Thermal ellipsoids are set to a 50% probability level and hydrogen atoms and outer sphere anions have been omitted for clarity.

The cobalt derivative **3.3** (Figure 3.5) exhibits a trigonal bipyramidal geometry that is unusual for an oxygen reduction catalyst. Cobalt ORR catalysts typically are square pyramidal.^{17,46} In complex **3.3**, TPA is again bound η_4 , with one triflate molecule bound directly to the metal center, giving a 17-electron complex. An additional triflate anion is present in the secondary coordination sphere, making **3.3** monocationic. In the case of **3.3**, the pyridyl arms are coordinated in a roughly symmetric fashion about the cobalt center. There is a slight distortion away from the coordinated triflate ion, as evidenced by the N2–Co–N4 angle of $118.2(2)^\circ$ (Table 3.1). This is also apparent in the τ value,⁴⁷ a common measure of the distortion from the idealized trigonal bipyramidal geometry, of $\tau = 0.95$.

Complex **3.3** is one of four 5-coordinate divalent cobalt TPA species, most of which have been studied for their magnetic properties.^{48,49} The bis(triflate) derivative structurally resembles previously reported $[\text{Co}(\text{TPA})\text{Cl}]^+$ cations.^{40,50} The Co–N_{amine} distance is the longest of the coordinated nitrogens at $2.162(5)$ Å, and the Co–N_{pyridine} distances are all identical within error ($2.039(5)$ Å). This is not the case with the manganese and iron derivatives and is presumably due to the lack of a significant trans effect from a sixth ligand coordinated trans to a pyridyl nitrogen. The Co–O_{OTf} distance is $2.016(4)$ Å. The values for reported chloride derivatives are significantly longer, displaying very weak interactions ($2.2759(6)$ and $2.279(2)$ Å respectively).^{41,50} This can be attributed to a better hard-hard pairing, as well as the presence of a delocalized π system present in the triflate ligand.

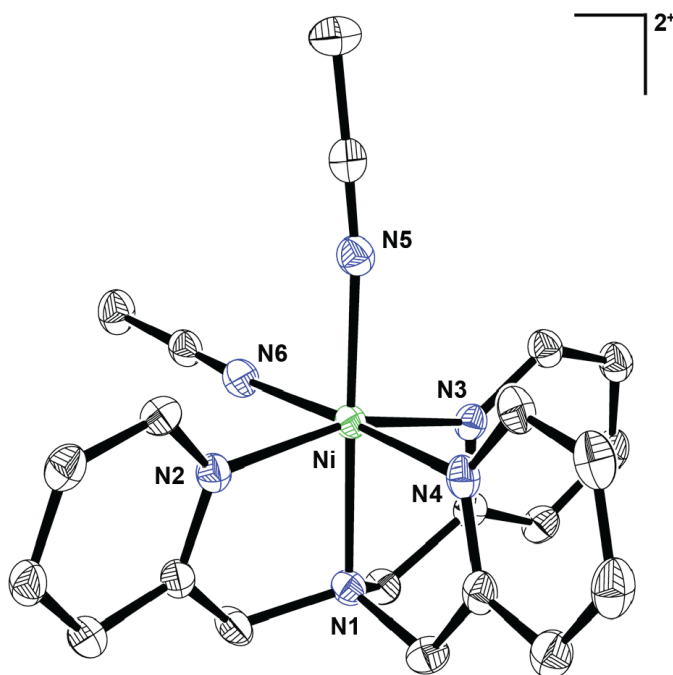


Figure 3.6. Molecular structure of nickel complex **3.4**. Thermal ellipsoids are set to a 50% probability level and hydrogen atoms and outer sphere anions have been omitted for clarity.

While not as common as the other first row metals presented in this work, there is some precedent for oxygen activation at nickel, although typically with softer ligands such as phosphines.²² Much like iron complex **3.4**, the nickel TPA triflate derivative **3.4** (Figure 3.6) possesses a roughly octahedral coordination environment, with two acetonitrile ligands bound to the metal center in addition to the η_4 -TPA. Two triflate anions are present in the outer coordination sphere, making the complex dicationic.

Species **3.4** is somewhat unusual in that it is a 20-electron complex. While not unprecedented for nickel(II) derivatives,⁵⁰ breaking the 18-electron rule does create a coordinatively saturated nickel center in **3.4** that makes substrate binding difficult. The electronic consequences of coordinating a sixth ligand are evidenced in the structural data. The Ni–Namine distance is similar to other divalent nickel TPA complexes at 2.090(2) Å.^{30,51} Interestingly however, the trans effects seen in the manganese and iron derivatives **3.1** and **3.2** are absent in **3.4**, with the pyridyl nitrogens all possessing, within error, identical bond lengths of 2.070(2) Å. The lack of trans effect is likely due to the labile nature of the second acetonitrile ligand, which if bound more strongly would inherently affect the bonding of the pyridyl nitrogen trans to it. This lability is demonstrated by the fact that although the pyridyl nitrogens lack any evidence of the trans effect, the two coordinated acetonitrile ligands display a dramatic difference in bond lengths (2.034(2) vs. 2.126(2) Å), with the weaker coordination again occurring trans to the pyridyl nitrogen of TPA. This weak coordination of the sixth ligand is seen in $[\text{Ni}(\text{Ph}_1\text{TPA})(\text{CH}_3\text{CN})_2](\text{ClO}_4)_2$ ⁵⁹ and $[\text{Ni}(\text{Me}_3\text{TPA})(\text{CH}_3\text{CN})_2](\text{ClO}_4)_2$,⁵³ both of which are dicationic 20-electron nickel complexes.

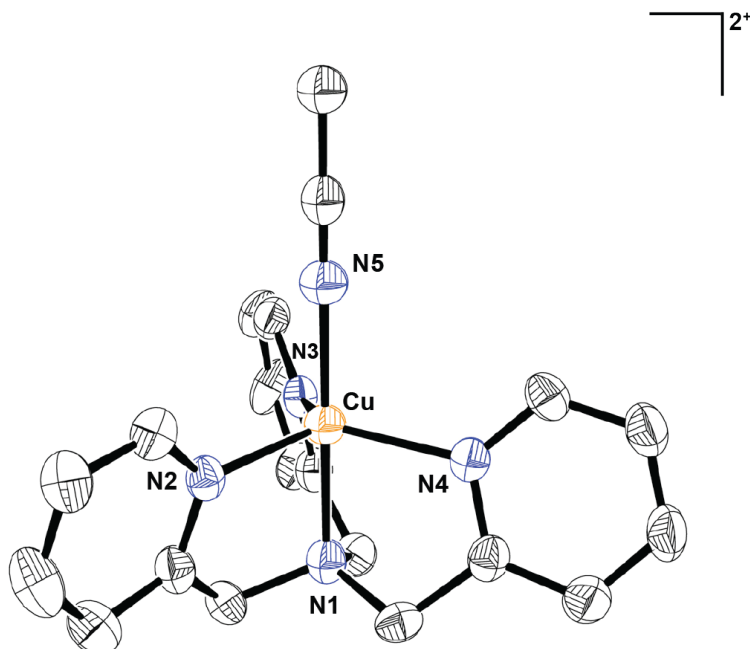


Figure 3.7. Molecular structure of copper complex **3.5**. Thermal ellipsoids are set to a 50% probability level and hydrogen atoms and outer sphere anions have been omitted for clarity.

The final complex in the triflate TPA series is the dicationic copper complex **3.5** (Figure 3.7). Copper derivatives of the TPA ligand have been studied for some time as blue copper protein mimics for oxygen activation and electron transfer reactions.^{10,54} The structural characteristics of **3.5** are similar to several isostructural dications present in the literature.^{25,55,56} Much like the cobalt derivative **3.3**, **3.5** employs a trigonal bipyramidal geometry ($\tau = 1.00$), with η_4 -TPA bound in a tripodal fashion, and an acetonitrile molecule occupying the remaining coordination site. Additionally there are two triflate anions in the secondary coordination sphere.

Complex **3.5** is highly symmetric, with one third of the molecule sitting on a C_3 element of symmetry that generates the rest (Table 3.2 contains relevant crystallographic data). Three of these symmetric one thirds are comprised in the asymmetric unit, and the Cu–N_{pyridine} distances given are an average of the three. Similar to several other copper TPA derivatives,^{25,57} the Cu–N_{amine} distance in **3.5** is 2.007(7) Å. Moving from **3.1** to **3.5**, this M–N_{amine} distance consistently decreases, apart from the iron complex **3.2**, which displays the shortest distance. This trend is in agreement with the Shannon ionic radii trends, as well as the those expected given the extra stabilization afforded via low-spin versus high-spin iron(II).⁵⁷

The Cu–N_{pyridine} distances are all equivalent (2.037(3) Å), with the N1–Cu–N5 line comprising a C_3 axis. In turn, each N_{pyridine}–Cu–N_{pyridine} angle is 120°, generated via crystallographic symmetry. Additionally, as in complexes **3.2** and **3.4**, the Cu–N_{MeCN} distance of 1.949(7) Å represents the shortest of the bound nitrogens, and is likely due to the better hard-hard pairing of the N-donor with the metal center.

Chapter 3

Table 3.2. Crystal and Refinement Data for Complexes **3.1–3.5**

Complex	3.1	3.2 ^a	3.3	3.4	3.5
empirical formula	C ₂₀ H ₁₈ F ₆ MnN ₄ O ₆ S ₂	C ₂₄ H ₂₄ F ₆ FeN ₆ O ₆ S ₂	C ₂₀ H ₁₈ CoF ₆ N ₄ O ₆ S ₂	C ₂₄ H ₂₄ F ₆ N ₆ Ni O ₆ S ₂	C ₂₄ H ₂₄ CuF ₆ N ₆ O ₆ S ₂
molecular weight	643.44	767.52	647.45	729.32	734.14
temp. (K)	130(2)	173(2)	100(2)	100(2)	121(2)
crystal system	monoclinic	monoclinic	orthorhombic	monoclinic	trigonal
space group	P2 ₁ /c	P2 ₁ /n	Pbca	P2 ₁ /n	P3c1
a (Å)	17.689(3)	12.418(2)	14.6412(14)	8.7494(4)	12.502(3)
b (Å)	9.7630(15)	16.192(4)	12.2822(11)	9.2921(4)	12.502(3)
c (Å)	16.092(2)	15.855(2)	28.154(3)	36.9208(17)	33.347(9)
α (deg)	90	90	90	90	90
β (deg)	113.203(2)	92.09(2)	90	95.994(2)	90
γ (deg)	90	90	90	90	120
volume (Å ³)	2554.2(7)	3585.8(10)	5062.8(8)	2985.3(2)	4514(2)
Z	4	4	8	4	6
λ (Å)	0.71073	0.71073	1.5418	1.54178	0.71073
μ (mm ⁻¹)	0.769	0.692	0.932	3.045	0.951
no. rflns measd	44420	6846	122621	19654	48764
no. indep rflns	4685	5616	4646	5303	5509
R _{int}	0.0493	0.0389	0.0351	0.0188	0.0471
Restr/param	0/352	0/433	0/352	0/408	1/422
R ₁ , wR ₂	0.0262,	0.0441,	0.0253,	0.0374,	0.0398,
R ₁ (all data)	0.0402	0.0657	0.0284	0.0404	0.0518
GOF	0.916	1.060	1.048	1.115	1.057

^aFor completeness, crystal and refinement data for **1.2** are appended from ref. 48.

Across the series **3.1–3.5**, and closely related to the manner in which O_2 is bound, each complex displays a geometry that is related to the intrinsic preference that each metal in a particular oxidation state possesses. High spin d^5 complexes adopt a tetrahedral geometry, however, in **3.1** coordination of the triflate ions yields a 17-electron complex. This is presumably more favorable than the 13-electron complex that would arise from a tetrahedral $Mn(TPA)$ dication. As seen in **3.2**, strong field ligands tend to form low-spin Fe^{2+} complexes that coordinate octahedrally to yield a closed shell.

The case of **3.4** is somewhat unusual in that adoption of an octahedral coordination environment affords a 20-electron complex. A d^8 metal is typically expected to employ a coordination number of either **3.4** or **3.5**, giving rise to a low-spin 16- or 18-electron complex respectively. However, due to electronegativity trends, the d orbitals of late transition metals are often low enough in energy to accommodate electrons in the antibonding e_g^* level. This is true for **3.4** and other TPA nickel adducts.^{52,58}

Cobalt(II) and copper(II) each possess 7 and 9 d electrons respectively, and in the case of **3.3** and **3.5** coordinate in a trigonal bipyramidal fashion. Complex **3.3** is one of the only pentacoordinate cobalt(II) complexes, two of which are other TPA derivatives, with the vast majority being either square pyramidal or octahedral.^{49,59} A trigonal bipyramidal coordination mode is typical for copper(II) species and in addition to **3.5**, is seen extensively in copper TPA chemistry.^{23,33} As with Ni^{2+} , the d orbitals are low enough in energy to accommodate electrons in antibonding orbitals. Decoordination of the ancillary ligand would give rise to a four-coordinate species capable of binding substrate via the respective d orbitals.

Magnetic Susceptibility. The magnetic susceptibility of each complex was determined in solution using the Evans' NMR method.⁶⁰ Except for **3.3**, all complexes displayed the spin states afforded via a simple crystal field splitting analysis. The colorless manganese complex **3.1** gave a μ_{eff} of 5.9(1) μ_B , corresponding to $S = 5/2$, as expected for high-spin Mn^{2+} . Iron complex **3.2** is red, as is typical of many low-spin Fe^{2+} complexes, and is diamagnetic.

The magnetism of complex **3.3** is different than predicted using a strict crystal field splitting analysis for cobalt(II) in a trigonal bipyramidal geometry. One unpaired electron is expected in the e' level. However, complex **3.3** gave a μ_{eff} of 4.2(1) μ_B , corresponding to $S = 3/2$. A likely explanation of this behavior lies with the ancillary ligand. The weak field nature of the triflate anion destabilizes its interaction with the metal center, causing the energy splitting to decrease, thus bringing the a_1' orbital to a comparable level with the e' orbitals. This molecular orbital picture yields three unpaired spins and is not unprecedented for cobalt(II) compounds in this geometry.^{61,62}

The nickel derivative **3.4** displays a distorted octahedral geometry, and as such the measured μ_{eff} of 2.9(1) μ_B , corresponding to $S = 1$, is consistent with the expected half-filled e_g^* level. Interestingly, this indicates that while the second coordinated acetonitrile is quite labile the formation of 20-electron complex **3.4** is not purely a crystal packing effect, as evidenced by the solution data. Copper complex **3.5** gave a μ_{eff} of 1.5(1) μ_B , corresponding to $S = 1/2$, which is coherent, as a d^9 metal possesses one unpaired spin no matter the coordination number.

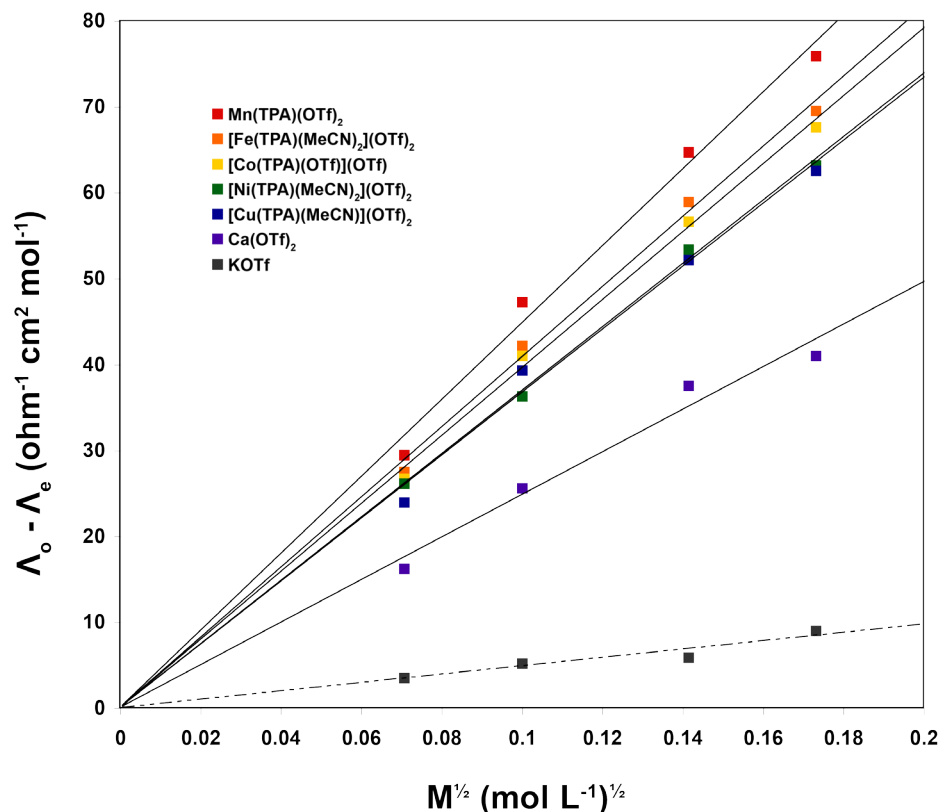


Figure 3.8. Onsager plots for complexes **3.1–3.5**, indicating 2:1 (—) and 1:1 (---) electrolytes respectively.

Conductance. Variable concentration conductance measurements were taken for each complex in the same solvent used to crystallize them: acetonitrile. Onsager plots of complexes **3.1–3.5** (Figure 3.8) were constructed and compared to electrolyte standards of both 1:1 (KOTf) and 2:1 (Ca(OTf)₂) triflate salts. In contrast to the structural trends observed in the solid-state, all compounds are 2:1 electrolytes in acetonitrile, meaning that the apparent preference for coordination of triflate versus acetonitrile is a solid-state packing effect. The magnetism data described above was also taken in acetonitrile, indicating that the geometry, and therefore coordination number, of each compound remains the same in solution. In the **3.1–3.5** series, acetonitrile has a high enough dielectric constant to support solvent separated ion pairs, and also appears in solution to coordinate to the manganese and cobalt complexes in place of triflate ions.

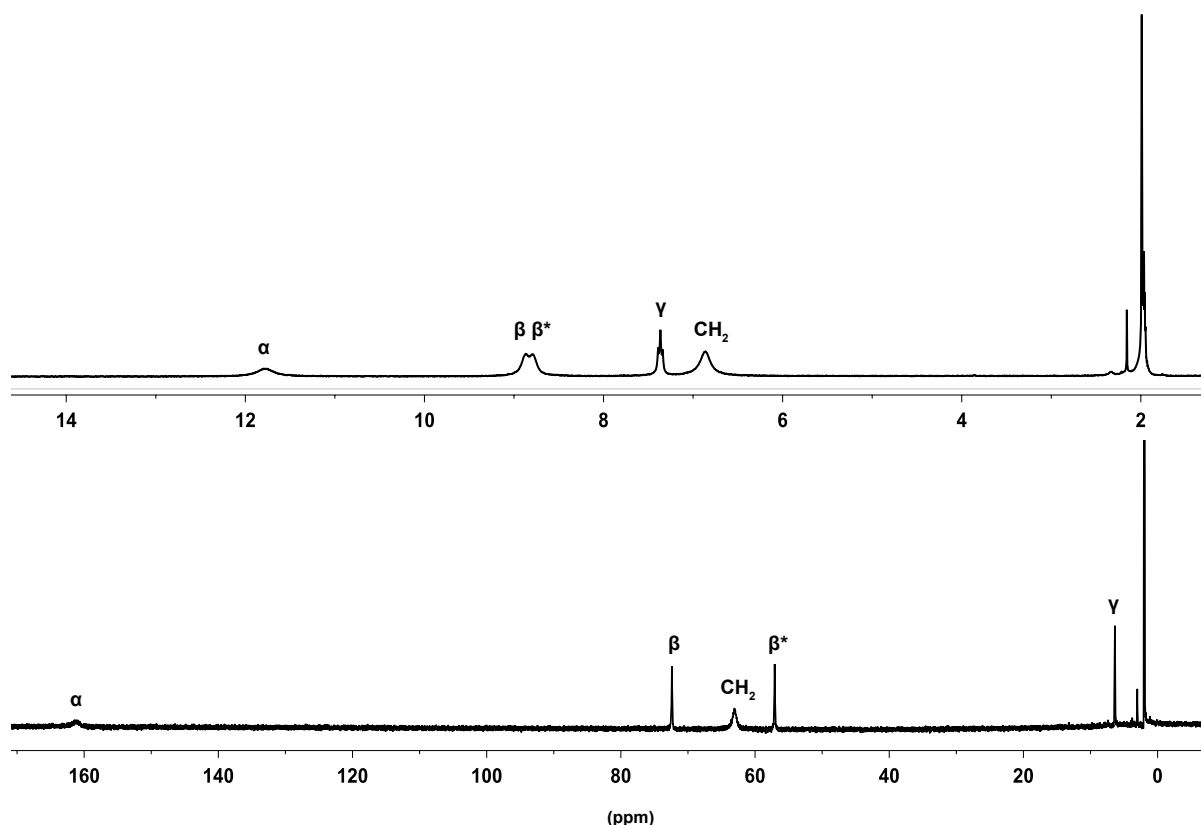


Figure 3.9. ^1H NMR spectra of **3.2** (top) and **3.3** (bottom), illustrating the five resonances that correspond to the protons of the pyridyl arms of the ligand, which are all equivalent in solution.

NMR Spectroscopy. The ^1H NMR data is consistent with the highly paramagnetic nature of the TPA triflate series **3.1–3.5**. The copper, nickel and manganese complexes all yield highly paramagnetically shifted, as well as broadened spectra. The cobalt complex gives a spectrum that is quite shifted but also sharp, and the iron complex yields resonances in the diamagnetic region (Figure 3.9). In complexes **3.2** and **3.3**, signals corresponding to each of the pyridyl protons as well as the methylene linker are easily discernable. The ^1H NMR spectra of both **3.2** and **3.3** possess five proton resonances, suggesting that the complexes have 3-fold symmetry with regard to the TPA ligand. On the timescale of the NMR experiment, there is an exchange between the pyridyl arms that averages their environments in solution, as has been observed with a related copper(I) TPA complex.⁶³

The spectrum of iron complex **3.2** is in the diamagnetic region, with the methylene protons giving a broad singlet at 6.88 ppm. The pyridyl proton resonances are shifted in accordance with their proximity to the metal center. The α proton, closest to the iron(II) center, is shifted the furthest downfield at 11.82 ppm (s), the two β protons give indiscernible overlapping singlets at 8.88 and 8.78 ppm respectively and the γ proton resonates at 7.32 ppm (s).

Likewise for cobalt complex **3.3**, there is fluxionality apparent in solution, as indicated by the presence of only five signals. Based on the relative ratios of the resonances, the peak at 63.08 ppm (s) is assigned to the methylene protons. The peak furthest downfield at 161.40 ppm (s) is assigned to the α pyridine proton. This is nearly analogous to the assignments made in **3.2**, and is consistent with the proximity of each proton to the paramagnetic Co(II) center. The β protons appear at 72.36 (s) and 57.04 ppm (s) respectively, and the γ proton resonates furthest upfield at 6.33 ppm (s).

Dynamic solution behavior is also evident in the ^{19}F NMR of complexes **3.1–3.5**, and concurs with the dicationic assignment made for the compounds via conductivity measurements. All five complexes display a single resonance, indicating an exchange between the two triflate anions present in each. Free triflate has an approximate fluorine resonance at -78 ppm.^{64,65} The fluorine resonances for the iron (-77.96 ppm), cobalt (-77.09 ppm), nickel (77.91 ppm) and copper (-78.25 ppm) complexes all indicate that neither triflate ion is bound to the metal center in solution. The resonance present in the manganese spectrum at -52.80 ppm seems to indicate an interaction with the metal center, but the highly paramagnetic nature of the complex and broadened signal, could also cause the shift.

Infrared Spectroscopy. The lability of the acetonitrile ligands bound to complexes **3.2**, **3.4** and **3.5** seen in the structural data is also evidenced in the solid-state IR. Free acetonitrile gives two stretches reported at 2292 and 2253 cm^{-1} .⁶⁶ As such, the iron complex **3.2** is expected to have four CN stretches, given the two acetonitrile ligands bound in the crystal structure, but it appears that the solvent is lost too quickly, and the corresponding IR stretches are unobserved. Additionally, the diamond anvil cell used for the IR measurements has a broad absorption around 2000 cm^{-1} that limits detection.⁶⁷ Therefore, the weak nature of the CN stretches observed in combination with the rapid loss of solvent could account for the lack of signals seen for **3.2**. For the nickel complex **3.4**, which has two acetonitrile ligands bound in the solid-state, there are four signals at 2324, 2307, 2295 and 2281 cm^{-1} . This is expected from the two signals that are attributed to two different IR active modes for free acetonitrile. Additionally, the copper complex **3.5** possesses two CN stretches at 2330 and 2299 cm^{-1} respectively, consistent with the one acetonitrile bound in the crystal structure.

Dioxygen Reactivity. In designing an ORR catalyst, it remains important to balance the need to not only bind and activate the O_2 bond, but in turn avoid the formation of a stable metal-oxo with the catalyst, as this would prevent further reduction and protonation. Thus, the reactivity of complexes **3.1–3.5** towards O_2 in the absence of protons and electrons was examined. Each divalent complex was reacted with a stoichiometric amount of dioxygen under the same conditions that electrochemical measurements were conducted.

Manganese complexes have not been as extensively studied for their oxygen reactivity as other first row derivatives. This is evidenced by the strikingly few number of structurally characterized Mn-dioxygen adducts.⁶⁸ Two notable examples are a manganese porphyrin and a Tp complex.^{69,70} Both bind O_2 in a side-on fashion and are thermally unstable at temperatures above -78 °C. However, an O_2 adduct is not observed with the TPA complex **3.1**, due most

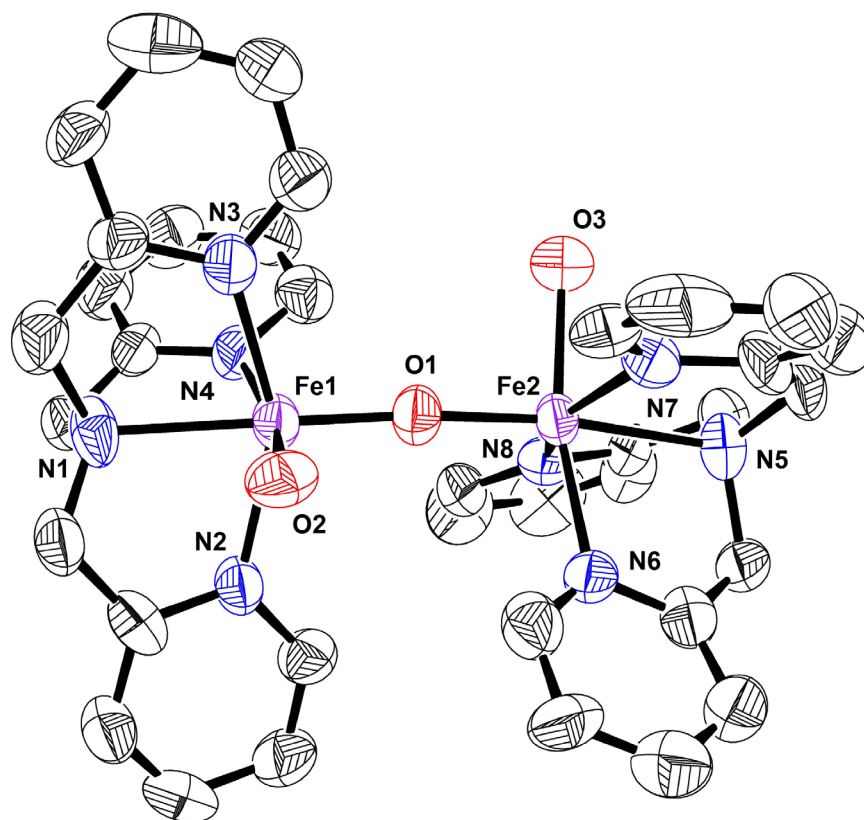
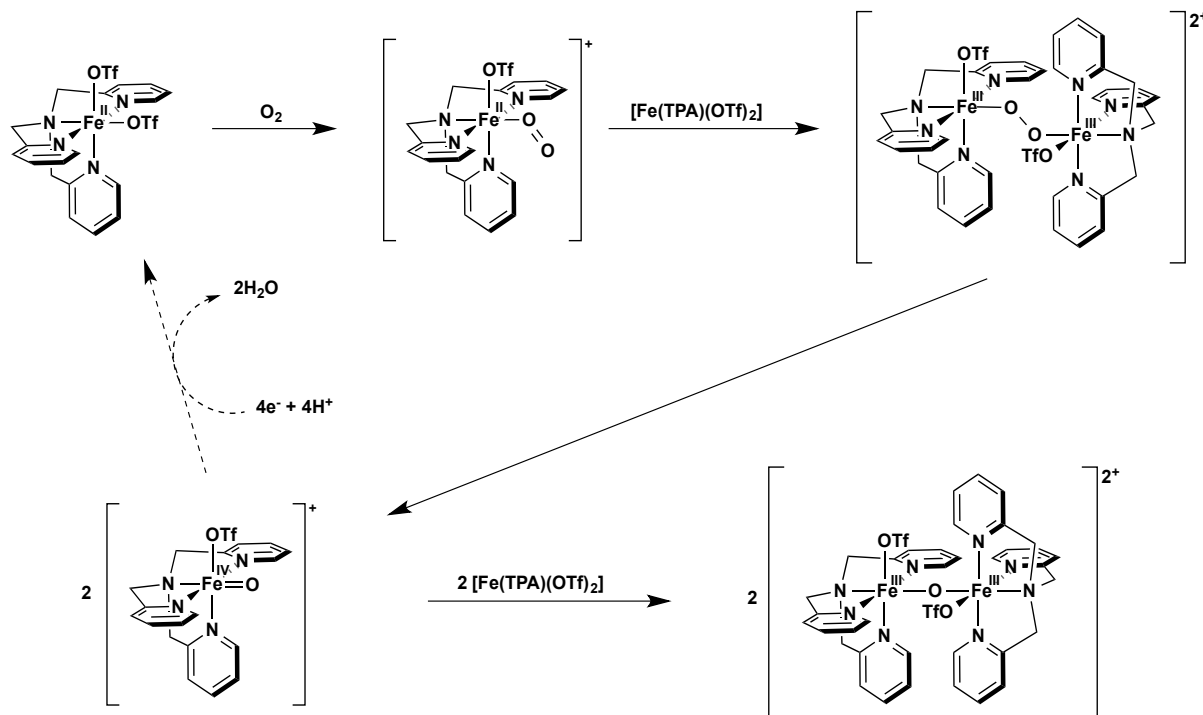


Figure 3.10. Molecular structure of μ -oxo iron dimer **3.6**. Thermal ellipsoids are set to a 50% probability level and hydrogen atoms have been omitted for clarity. Bound triflate anions have been truncated to coordinated oxygens O2 and O3 for clarity. Select bond lengths (Å) and angles (°): Fe1–O1, 1.766(3); Fe2–O1, 1.814(3); Fe1–O2, 2.124(4); Fe2–O3, 2.127(4); Fe1–N1, 2.219(4); Fe1–N2, 2.122(4); Fe1–N3, 2.099(5); Fe1–N4, 2.157(5); Fe2–N5, 2.229(4); Fe2–N6, 2.147(5); Fe2–N7, 2.177(4); Fe2–N8, 2.142(4); Fe1–O–Fe2, 174.6(2); N3–Fe1–N4, 82.4(2); N3–Fe1–N1, 77.3(2); N6–Fe2–N7, 83.6(2); N6–Fe2–N5, 76.9(2).

likely to the fact that binding is labile at ambient temperature. Additionally, some manganese complexes, such as Mn salphen, react with oxygen to form highly stable μ -oxo dimers.⁶⁹ Yet, likely due to the starkly different coordination environment, this behavior is not observed for complex **3.1**, as no Mn-oxo products were isolated from its reaction with dioxygen.

When trying to reduce oxygen to water using an iron catalyst, side reactions leading to the formation of thermodynamically stable iron-oxos are problematic. Complex **3.2** proves to have such behavior. Reaction of **3.2** with dioxygen followed by filtration and recrystallization from acetonitrile yielded $[(\text{TPA})_2\text{Fe}_2(\mu\text{-O})(\text{OTf})_2](\text{OTf})_2$ (**3.6**) in 66% yield (Figure 3.10). The generation of μ -oxos from the reaction of dioxygen and iron complexes is very common in porphyrin chemistry via the “autooxidation mechanism” and has been more generally applied to analogous iron TPA systems as well.^{45,71} Adapting the autooxidation mechanism for the formation of **3.6** we propose a plausible mechanism where an initial binding of O_2 is followed

Scheme 3.2. Potential Autooxidation Mechanism for the Formation of **3.6** and Associated Issues for Catalytic Oxygen Reduction.



by dimerization with another iron center to yield an iron(III)/iron(III) peroxo species. Further activation of oxygen results in a highly reactive iron(IV) oxo species which rapidly undergoes dimerization with another equivalent of iron starting compound to yield final μ -oxo species (Scheme 3.2). Of note is that the formation of the thermodynamically stable μ -oxo species **3.6** is in direct competition with the desired reactivity pathway (indicated with dotted lines in Scheme 3.2) for ORR whereby protons and electrons combine with any highly reactive intermediate to release water and regenerate the catalyst.

The solid-state structural characteristics of **3.6** (Figure 3.10) are similar to those presented for a series of related chloride derivatives.²⁷ The Fe1–O–Fe2 angle is nearly linear ($174.6(2)^\circ$). Two triflate molecules are directly bound to the dimer, with two present in the outer coordination sphere. One coordinated triflate molecule is disordered and was modeled accordingly (only one occupancy is depicted for clarity). The magnetic susceptibility is $3.2(1) \mu_{\text{B}}$ for **3.6**, corresponding to high-spin iron(III) centers which are antiferromagnetically coupled, similar to other oxo dimers of iron.⁷³

Divalent cobalt complexes such as cobalt salen are well known for their ability to reversibly bind O_2 . Additionally, the propensity of cobalt complexes, such as cobalt porphyrins, to reduce oxygen to water has been examined.¹⁷ None-the-less, we are unaware of reports of cobalt TPA complexes being investigated for such reactivity. Neither oxygen binding, nor oxygen activation under ambient conditions were observed with complex **3.3**. As with the manganese complex **3.1**, it is possible that a facile exchange with O_2 as a ligand is occurring, but that it is too weak to observe at room temperature.

Reaction of the nickel and copper complexes **3.4** and **3.5** with oxygen returned only starting material. This is as expected for these metals in their divalent states. Nickel(I) complexes have been shown to react with dioxygen,⁷³ however the only reactivity towards oxygen seen with nickel(II) species was with the diphosphine complex mentioned earlier.²² It is thus not surprising that complex **3.4** showed no reactivity towards O_2 . Similarly, copper(I) complexes are known to react readily with oxygen, much like the blue copper proteins. Copper TPA systems have been studied for this activity and it has been shown that copper(II) species must be reduced either chemically or electrochemically before a reaction with oxygen is observed.¹⁹ Therefore it is logical that the copper(II) species **3.5** did not show an interaction with dioxygen.

The desired reactivity for the series **3.1–3.5** is the catalytic four-electron reduction of oxygen to water. Any alternate pathway that is kinetically or thermodynamically favorable will greatly reduce the turnover of the catalyst, as well as generate undesirable side products that may interfere with the environment of the fuel cell. For this divalent series, only **3.2** appears to have a thermodynamic metal-oxo sink.

Conclusions

A series of simple first row complexes $[(TPA)M^{2+}]^{n+}$ ($M = Mn, Fe, Co, Ni$ and Cu) have been prepared and their solution and solid-state properties detailed. X-ray diffraction studies reveal each complex to have subtle differences in coordination environment that vary in accordance with the metal center involved. However, conductance measurements indicate that all complexes are dicationic in solution, suggesting that the coordination preferences seen in the crystal structures are the result of solid-state effects. Further characterization of **3.1–3.5** by infrared spectroscopy, 1H and ^{19}F NMR spectroscopy and magnetic susceptibility provide details that serve as a molecular standard of comparison for hybrid materials. This series offers a unique opportunity to systematically study how the characteristics of a series of complexes known to have desired ORR activity vary in accordance with the metal center. Only the iron complex **3.2** shows undesired formation of a thermodynamic μ -oxo sink upon reaction with dioxygen. As compared to platinum-based solid-state catalysts, this series of TPA complexes represents a low-cost alternative that is straightforward to synthesize, characterize and tune for desired properties. The electrochemistry and implementation of these complexes as oxygen reduction catalysts in membrane electrode assemblies is detailed in chapter 4.

Experimental Section

General Procedures. Unless otherwise noted, all reactions were performed using standard Schlenk line techniques or in an MBraun N₂-atmosphere glovebox (< 1 ppm O₂/H₂O). All glassware, cannulae and Celite were stored in an oven at ~ 150 °C. Diethyl ether, tetrahydrofuran and dichloromethane were dried by passing over an activated alumina column and degassed with nitrogen prior to use.⁷⁴ Acetonitrile was distilled from P₂O₅ and degassed prior to use. *n*-butanol was dried over 4 Å sieves and degassed prior to use. Deuterated solvents (CD₃CN and CDCl₃) were vacuum-transferred from CaH₂ and degassed with three freeze-pump-thaw cycles. All NMR spectra were recorded at ambient temperature on Bruker AVQ-300, AVQ-400 or AVB-400 spectrometers. ¹H chemical shifts (δ) are given relative to residual solvent peaks. ¹⁹F chemical shifts (δ) were referenced to an external standard (CFCl₃ at 0.00 ppm). Infrared (IR) spectra were recorded with a Thermo Scientific Nicolet iS10 FTIR spectrophotometer either as powder, or as Nujol mulls between KBr plates. Magnetic susceptibility (μ_{eff}) values were determined in CD₃CN using the Evans' NMR method⁶⁰ at ambient temperature (25 °C). Electrical conductivity measurements were carried out in MeCN using a VWR symphony meter, model SB80PC, with an epoxy body two cell platinum conductivity probe, model 11388-372. The cell constant was determined using a standard aqueous KCl solution. Conductivity measurements taken at various concentrations were used to construct Onsager plots of complexes **3.1–3.5**, and compared to standard 1:1 and 2:1 electrolytes.^{54,88} Melting points were determined using sealed capillaries prepared under nitrogen and are uncorrected. Elemental analyses were determined at the Microanalytical Facility at the College of Chemistry, University of California, Berkeley. X-ray structural determinations were performed at CHEXRAY, University of California, Berkeley, on Bruker SMART 1000, SMART APEX, or MicroSTAR-H X8 APEXII diffractometers. The previously reported synthesis for tris[(2-pyridyl)methyl]amine¹⁰ (TPA) did not yield consistent results in our hands, so an alternative procedure is given below. [(TPA)Fe(MeCN)₂](OTf)₂,⁴¹ was prepared by an alternative procedure given below. (TPA)CoCl₂ was made according to previously reported literature procedure.⁴⁰ The remaining starting materials were obtained from commercial sources and used without further purification.

Tris(2-pyridylmethyl)amine (TPA). To a suspension of NaI (6.85 g, 0.046 mol) and Cs₂CO₃ (29.8 g, 0.091 mol) in 100 mL MeCN was added 2-(chloromethyl)pyridine hydrochloride (5.0 g, 0.03 mol) to produce an orange suspension. To the reaction mixture was added 2-picolyamine (1.57 mL, 0.015 mol). The mixture was stirred vigorously for 48 h and monitored by TLC (9:1 DCM:MeOH, 1% Et₃N). The reaction mixture was filtered and the solids washed (3 × 100 mL) with MeCN to give an orange solution. The extracts were combined and the solvent removed in vacuo to yield a red solid. The solid was extracted with Et₂O (3 × 25 mL) and chilled overnight at -40 °C to afford the product as colorless blocks (2.68 g, 61% yield).

(TPA)Mn(OTf)₂ (3.1). A solution of TPA (333 mg, 1.15 mmol) in 10 mL MeCN was added to a solution of Mn(OTf)₂ (405 mg, 1.15 mmol) in 10 mL of MeCN to produce a pale yellow solution. After stirring at RT for 12 h, the reaction mixture was filtered to yield a yellow solution. The filtrate was concentrated until it became viscous and Et₂O was carefully layered on top to give colorless blocks via diffusion induced precipitation over 24 h (576 mg, 78%

yield). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of Et₂O into **3.1** in MeCN. ¹H NMR (300 MHz, CD₃CN, 22 °C) δ 53.46 (br, s), 51.24 (br, s), 14.59 (br, s). ¹⁹F NMR (400 MHz, CD₃CN, 22 °C) δ -52.80 (s, br, OTf). IR (cm⁻¹): 1609 (m), 1576 (w), 1484 (w), 1446 (s), 1317 (s), 1296 (m), 1243 (s), 1216 (s), 1166 (m), 1101 (w), 1055 (w), 1036 (s), 1020 (m), 907 (w), 800 (w), 768 (m), 760 (m), 723 (w), 636 (s). Anal. Calcd (%) for C₂₀H₁₈F₆MnN₄O₆S₂: C, 39.52; H, 3.32; N, 11.53. Found: C, 39.66; H, 3.46; N, 11.34. Mp: 174.2–174.8 °C. $\mu_{\text{eff}} = 5.9(1) \mu_{\text{B}}$.

[(TPA)Fe(MeCN)₂](OTf)₂ (3.2). A solution of TPA (200 mg, 0.69 mmol) in 2 mL MeCN was added to a suspension of Fe(OTf)₂ (244 mg, 0.69 mmol) in 5 mL of MeCN to produce a red suspension. After stirring at room temperature for 1 h, the reaction mixture was filtered to yield a red solution. Et₂O was added to the filtrate to precipitate the previously reported compound as a red microcrystalline solid. (440 mg, 88% yield). ¹⁹F NMR (400 MHz, CD₃CN, 22 °C) δ -77.96 (s, OTf). IR (cm⁻¹): 1608 (m), 1574 (w), 1486 (w), 1467 (w), 1445 (m), 1262 (s), 1221 (s), 1153 (s), 1100 (m), 1026 (s), 908 (w), 818 (m), 763 (s), 735 (m). Mp: dec. > 90.9 °C.

[(TPA)Co(OTf)](OTf) (3.3). A solution of (TPA)CoCl₂ (420 mg, 1.0 mmol) in 20 mL of MeCN was added via cannula to a suspension of Ag(OTf) (61 mg, 3.0 mmol) in 20 mL of MeCN to produce a pink-purple suspension. After stirring at room temperature for 15 min, the reaction mixture was filtered through Celite to yield a dark pink-purple solution. The filtrate was concentrated until it became viscous and Et₂O was carefully added until the product began to crystallize. The solution was then chilled overnight at -40 °C to afford the product as grey-purple needles (620 mg, 96% yield). Single crystals suitable for X-ray diffraction were obtained by vapor diffusion of Et₂O into a concentrated solution of **3.3** in MeCN. ¹H NMR (300 MHz, CD₃CN, 22 °C) δ 161.40 (s), 72.36 (s), 63.08 (br, s), 57.04 (s), 6.33 (s). ¹⁹F NMR (400 MHz, CD₃CN, 22 °C) δ -77.09 (s, OTf). IR (cm⁻¹): 1614 (m), 1574 (w), 1487 (w), 1446 (m), 1326 (m), 1302 (s), 1266 (m), 1208 (m), 1170 (m), 1106 (w), 1058 (w), 1029 (s), 1003 (w), 976 (w), 782 (w), 765 (m), 734 (w), 637 (m). Anal. Calcd (%) for C₂₀H₁₈CoF₆N₄O₆S₂: C, 37.10; H, 2.80; N, 8.65. Found: C, 36.76; H, 2.98; N, 8.37. Mp: dec. > 160.0 °C. $\mu_{\text{eff}} = 4.2(1) \mu_{\text{B}}$.

[(TPA)Ni(MeCN)₂](OTf)₂ (3.4). A solution of TPA (50 mg, 0.17 mmol) in 3 mL of MeCN was added to a solution of Ni(OTf)₂ (61 mg, 0.17 mmol) in 3 mL of MeCN to produce a pale yellow suspension. After stirring at RT for 72 h, the reaction mixture was filtered to yield a pink solution. The filtrate was concentrated until it became viscous and Et₂O was carefully layered on top to give pink-purple needles via diffusion induced precipitation over 24 h (108 mg, 87% yield). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of Et₂O into **3.4** in MeCN. ¹H NMR (300 MHz, CD₃CN, 22 °C) δ 53.46 (br, s), 51.24 (br, s), 14.59 (br, s). ¹⁹F NMR (400 MHz, CD₃CN, 22 °C) δ -77.91 (s, OTf). IR (cm⁻¹): 2324 (w, CN), 2307 (w, CN), 2295 (w, CN), 2281 (w, CN), 1609 (m), 1259 (s), 1225 (m), 1144 (s), 1102 (w), 1056 (w), 1030 (s), 975 (w), 945 (w), 912 (w), 785 (m), 756 (m), 736 (w), 723 (w), 637 (s), 573 (m), 517 (m). Anal. Calcd (%) for C₂₄H₂₄F₆N₆NiO₆S₂: C, 39.52; H, 3.32; N, 11.53. Found: C, 39.66; H, 3.46; N, 11.34. Mp: dec. > 77.0 °C. $\mu_{\text{eff}} = 2.9(1) \mu_{\text{B}}$.

[(TPA)Cu(MeCN)](OTf)₂•(MeCN) (3.5). A solution of TPA (300 mg, 1.0 mmol) in 10 mL of MeCN was added to a solution of Cu(OTf)₂ (374 mg, 1.0 mmol) in 10 mL of MeCN to produce a dark blue solution. After stirring at RT for 2 h, the reaction mixture was filtered and the filtrate was concentrated until it became viscous. Et₂O was carefully layered on top to give blue hexagonal crystals via diffusion induced precipitation over 24 h (620 mg, 87% yield). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of Et₂O into **3.5** in MeCN. ¹H NMR (400 MHz, CD₃CN, 22 °C) δ 30.99 (br, s), 10.70 (br, s). ¹⁹F NMR (400 MHz, CD₃CN, 22 °C) δ -78.25 (s, OTf). IR (cm⁻¹): 2330 (m, CN), 2299 (m, CN), 1609 (m), 1255 (s), 1221 (m), 1150 (s), 1195 (w), 1031 (s), 974 (w), 955 (w), 907 (w), 770 (m), 757 (w), 722 (w), 638 (s), 573 (m), 518 (m), 505 (w). Anal. Calcd (%) for C₂₄H₂₄CuF₆N₆O₆S₂: C, 39.26; H, 3.30; N, 11.45. Found: C, 39.20; H, 3.50; N, 11.15. Mp: dec. > 79.6 °C. μ_{eff} = 1.5(1) μ_B.

[(TPA)₂Fe₂(μ-O)(OTf)₂](OTf)₂ (3.6). Using a known volume bulb, O₂ (6.9 mL, 0.28 mmol) was introduced to a solution of **3.2** (138 mg, 0.19 mmol) in 10 mL of DCM, giving a yellow solution. After stirring for 48 h, a pale orange precipitate had formed. Following filtration, the solid was dissolved in MeCN, concentrated until viscous and Et₂O was carefully layered on top to give microcrystalline red blocks via diffusion induced precipitation over 24 h (40 mg, 66% yield). Single crystals suitable for X-ray diffraction were obtained by vapor diffusion of Et₂O into **3.6** in MeCN. ¹H NMR (400 MHz, CD₃CN, 22 °C) δ 30.65 (br, s), 18.65 (br, s), 6.17 (br, s). ¹⁹F NMR (400 MHz, CD₃CN, 22 °C) δ -74.22 (br, s, OTf). IR (cm⁻¹): 1609 (m), 1574 (w), 1488 (w), 1446 (w), 1325 (m), 1259 (s), 1235 (s), 1202 (s), 1154 (s), 1102 (m), 1059 (m), 1026 (s), 1010 (s), 908 (w), 817 (s), 764 (s), 725 (m). Anal. Calcd (%) for C₄₀H₃₆F₁₂Fe₂N₈O₁₃S₄: C, 36.82; H, 2.78; N, 8.59. Found: C, 37.10; H, 2.97; N, 8.34. Mp: dec. > 190.1 °C. μ_{eff} = 3.2(1) μ_B.

Crystallographic Analyses. Single crystals of compounds **3.1** and **3.3–3.6** were coated in Paratone-N oil and mounted on a Kapton loop. The loop was transferred to either a Bruker SMART 1000, SMART APEX, or MicroSTAR-H X8 APEXII diffractometer equipped with a CCD area detector,⁷⁵ centered in the beam, and cooled by an Oxford Cryostream 700 LT device that has been previously calibrated by a thermocouple placed at the same position as the crystal. Preliminary orientation matrixes and cell constants were determined by collection of 60, 30 s frames, followed by spot integration and least-squares refinement. An arbitrary hemisphere of data was collected and the raw data were integrated using SAINT.⁷⁶ Cell dimensions reported were calculated from all reflections with *I* > 10σ. The data were corrected for Lorentz and polarization effects; no correction for crystal decay was applied. Data were analyzed for agreement and possible absorption using XPREP.⁷⁷ An empirical absorption correction based on comparison of redundant and equivalent reflections was applied using SADABS.⁷⁸ The structures were solved using SHELXS⁷⁹ and refined on all data by full-matrix least-squares with SHELXL-97.⁸⁰ Thermal parameters for all non-hydrogen atoms were refined anisotropically. ORTEP diagrams were created using ORTEP-3.⁸¹ Compound **3.6** possessed highly disordered outer sphere acetonitrile molecules, and the data was treated with the SQUEEZE routine included in PLATON.⁸¹

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Chapter 3

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Chapter 4

Electrocatalytic Four-Electron Dioxygen Reduction by a Series of Nonprecious Transition Metal Complexes

Overview

The electrocatalytic reduction of dioxygen is a reaction of fundamental importance to fuel cell technologies. Recent efforts to employ molecular alternatives to solid-state catalysts have focused on transition metal complexes that mimic the coordination environment of oxygen activating enzymes. Chapter 3 detailed the synthesis and characterization of a series of first row transition metal complexes supported by the tris(2-pyridylmethyl)amine ligand and intended for this purpose. The following chapter expands upon this work, and describes the solution electrochemical behavior of this group of TPA complexes, as well as their performance as electrocatalysts for oxygen reduction on a carbon support in Nafion. Portions of this chapter have previously been published in: Ward, A. L., Elbaz, L., Kerr, J. B., and Arnold, J. "Nonprecious Metal Catalysts for Fuel Cell Applications: Electrochemical Dioxygen Activation by a Series of First Row Transition Metal Tris(2-pyridylmethyl)amine Complexes." *Inorg. Chem.*, **2012**, *51*, 4694.

Introduction

The mediation of dioxygen activation by transition metals is a chemical transformation with a wide variety of synthetic and biological significance.¹⁻¹⁰ One application of particular interest lies in energy conversion technologies, where the electrochemical four-electron reduction of dioxygen to water is utilized in proton exchange membrane fuel cells (Figure 4.1).¹¹⁻¹⁵ While

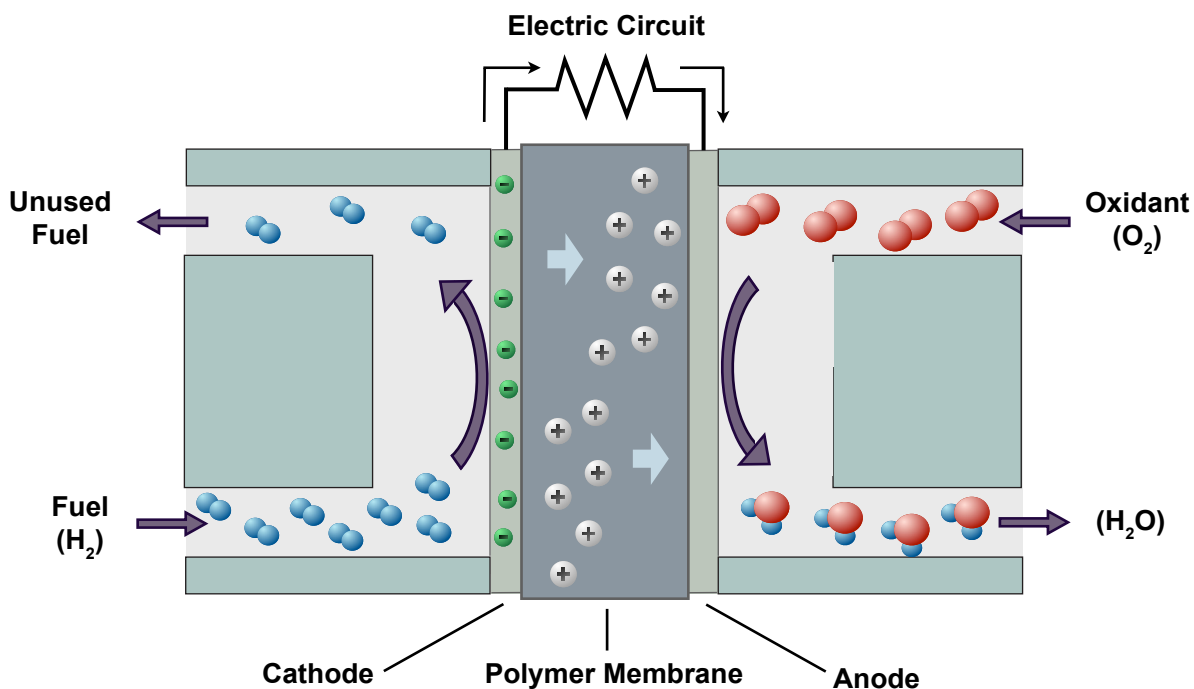


Figure 4.1. Diagram of a proton exchange membrane fuel cell (PEMFC).

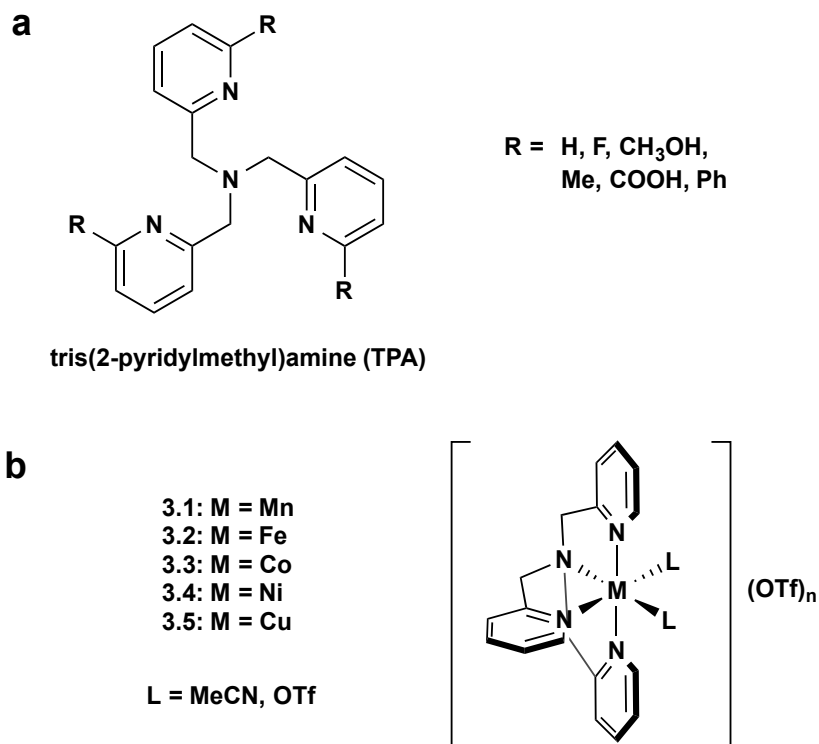


Figure 4.2. Ligand system of interest and complexes studied for electrocatalytic oxygen reduction. a) Tris(2-pyridylmethyl)amine (TPA) ligand and various derivatives.^{35–40} b) Series of first row transition metal complexes investigated as electrocatalysts (**3.1–3.5**).

thermodynamically very favorable, the oxygen reduction reaction (ORR) is currently mediated by platinum-based electrocatalysts, whose high cost, scarcity and kinetic inefficiencies have hindered fuel cell commercialization.^{11,12,16,17} It is therefore desirable to study nonprecious metal catalysts capable of four-proton and four-electron ORR via a selective and complete pathway.

Traditionally, solid-state materials have been incorporated as electrocatalysts in PEMFCs.^{12,17–20} However, the use of transition metal coordination compounds as ORR catalysts has gained interest in recent years.^{13,15,21,22} This is due to the ability to accurately characterize the catalytic active site and in turn tune reactivity. In a biomimetic approach to the design of such synthetic systems, attempts have been made to emulate the active sites of oxygen binding and activating enzymes such as heme/copper oxidases, which selectively and efficiently catalyze the conversion of O₂ to H₂O in the final stages of cellular respiration.^{4,23–26} The active sites of these and related proteins often involve a transition metal bound by a tripodal nitrogen coordination sphere. As such, one system often utilized as a synthetic mimic is that of the ligand tris(2-pyridylmethyl)amine (TPA) (Figure 4.2a).^{10,12,25,27,28} Iron and copper derivatives of TPA have been studied as O₂ activation catalysts for some time, as they are the two transition metal ions most often utilized in nature for manipulating oxygen.^{10,25,29–32} A copper TPA complex has been employed as promising molecular ORR electrocatalyst with an onset potential of 0.53 V vs. SHE.³³ There is also recent literature precedent for electrocatalytic O₂ reduction by a copper

(II) complex immobilized on an electrode surface.³⁴ However, the oxygen reduction reactivity and electrocatalysis of other transition metal complexes of TPA have not been reported. Additionally, although many first row coordination compounds exhibit a propensity for oxygen activation and reduction, there has been no systematic study of the effect of varying the metal center within a standard coordination environment.

In an attempt to address this deficiency, a simple molecular system capable of ORR and compatible with a fuel cell environment was selected for study. As previously detailed, the TPA scaffold has been shown to support complexes capable of oxygen activation, and in chapter 3 a series of transition metal TPA complexes [(TPA)M²⁺]ⁿ⁺ (M= Mn, Fe, Co, Ni and Cu) (**3.1–3.5**, respectively) suitable for this type of study were presented (Figure 4.2b). The triflate counter anions present in these complexes are weakly coordinating, providing the possibility for open coordination sites, and closely resemble the terminal perfluoroalkylsulfonate anions present in the Nafion polymer electrolyte membrane, making complexes **3.1–3.5** particularly suitable as molecular ORR catalysts for fuel cells.^{41,42} The solution and solid-state electrochemical behavior of complexes **3.1–3.5** is presented and their electrocatalytic oxygen reduction performance—both in solution and on a carbon support in Nafion—is described.

Results and Discussion

Cyclic Voltammetry. Given the eventual goal of employing complexes **3.1–3.5** as electrocatalysts, their electrochemical behavior was first ascertained using cyclic voltammetry (CV) in acetonitrile with 0.1 M (nBu₄N)(PF₆) as the supporting electrolyte, and an Ag/Ag⁺ reference. The CVs of the iron and copper complexes show reversible one-electron redox waves (Figures 4.4 and 4.7). In contrast, the manganese, cobalt and nickel complexes reveal more complicated electrochemical behavior (Figures 4.3, 4.5 and 4.6).

Table 4.1. Cyclic Voltammetry Data for Complexes **3.1–3.5**^a

Complex	E _{pc} ^b	E _{pa} ^c	E _{1/2} ^d	Redox Couple
3.1	-	1.79	-	Mn ³⁺ /Mn ²⁺
3.2	1.11	1.19	1.15	Fe ³⁺ /Fe ²⁺
3.3	-1.15	-1.03	-1.09	Co ²⁺ /Co ¹⁺
3.4	-1.15	-1.00	-1.08	Ni ²⁺ /Ni ¹⁺
3.5	0	0.06	0.03	Cu ²⁺ /Cu ¹⁺

^aMeasurements taken under inert atmosphere in MeCN at 25 °C with 1 mM complex (5 mM of **3.1**) and 0.1 M (nBu₄N)(PF₆). ^bCathodic peak potential (V vs. Ag/Ag⁺). ^cAnodic peak potential (V vs. Ag/Ag⁺). ^dHalf-wave potential (V vs. Ag/Ag⁺).

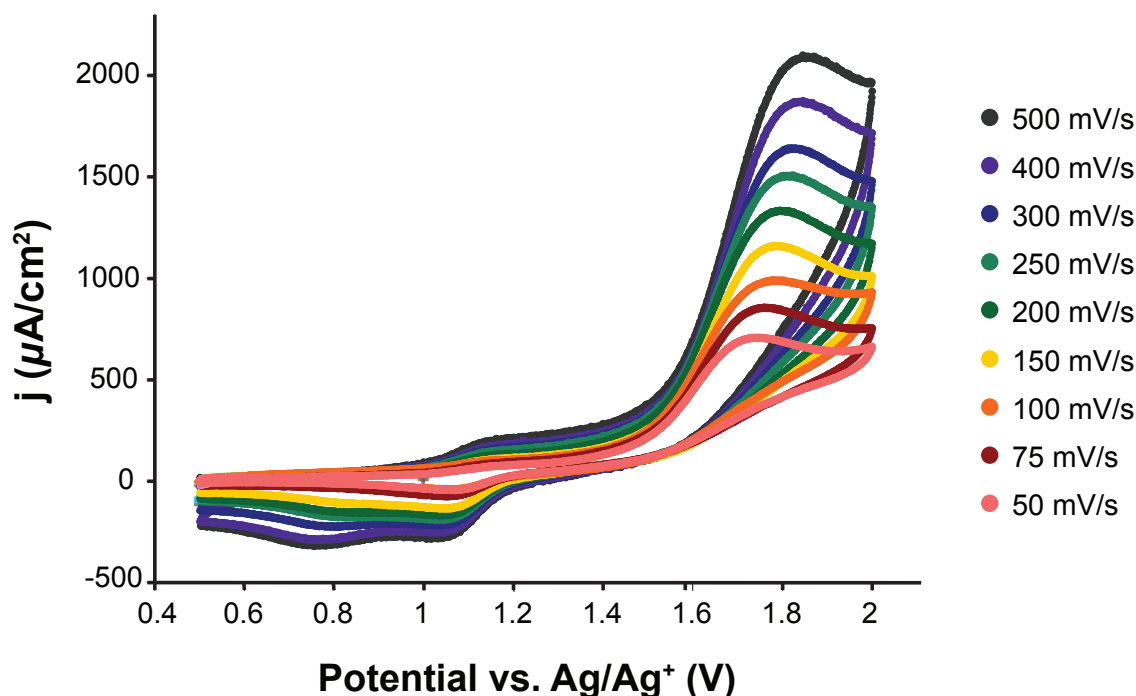


Figure 4.3. Variable scan rate cyclic voltammogram of complex **3.1** (5 mM) in MeCN, 25 °C.

The voltammogram of **3.1** shows an irreversible one-electron oxidation wave at 1.79 V (E_{pa} , Table 4.1). This wave is assigned to a metal-based $\text{Mn}^{3+}/\text{Mn}^{2+}$ oxidation. The process is irreversible even with increasing scan rate (Figure 4.3), indicating that the redox event is followed by an irreversible chemical reaction.

Characteristic of many iron(II) complexes, complex **3.2** displays a reversible one-electron oxidation at 1.15 V ($E_{1/2}$, Table 4.1). These waves are assigned to a reversible $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple (Figure 4.4). The redox potential of **3.2** is significantly more positive (0.8 V or more) than that of similar iron TPA complexes.⁴³ This is likely due to the high-spin low-spin nature of the complex in question, as a high-spin iron(II) complex is expected to be much easier to oxidize than a low-spin iron(II) complex.

Cobalt complex **3.3** displays unusual electrochemical behavior (Figure 4.5). Oxygen reduction chemistry involving cobalt often employs a $\text{Co}^{2+}/\text{Co}^{3+}$ redox couple, however these redox states are not observed in the solution CV. On the reductive side of the voltammogram, there is a quasi-reversible wave ($E_{1/2}$, Table 4.1) corresponding to a one-electron reduction. This is a metal-based reduction that is attributed to a $\text{Co}^{2+}/\text{Co}^{1+}$ couple. Interestingly, at low scan rates the wave is almost completely irreversible, but at faster scan rates the wave approaches reversibility. This phenomenon has been observed with a bipyridyl cobalt system and is attributed to an EC (electrochemical/chemical) process that is only observed for certain scan rates in the CV.⁴⁴

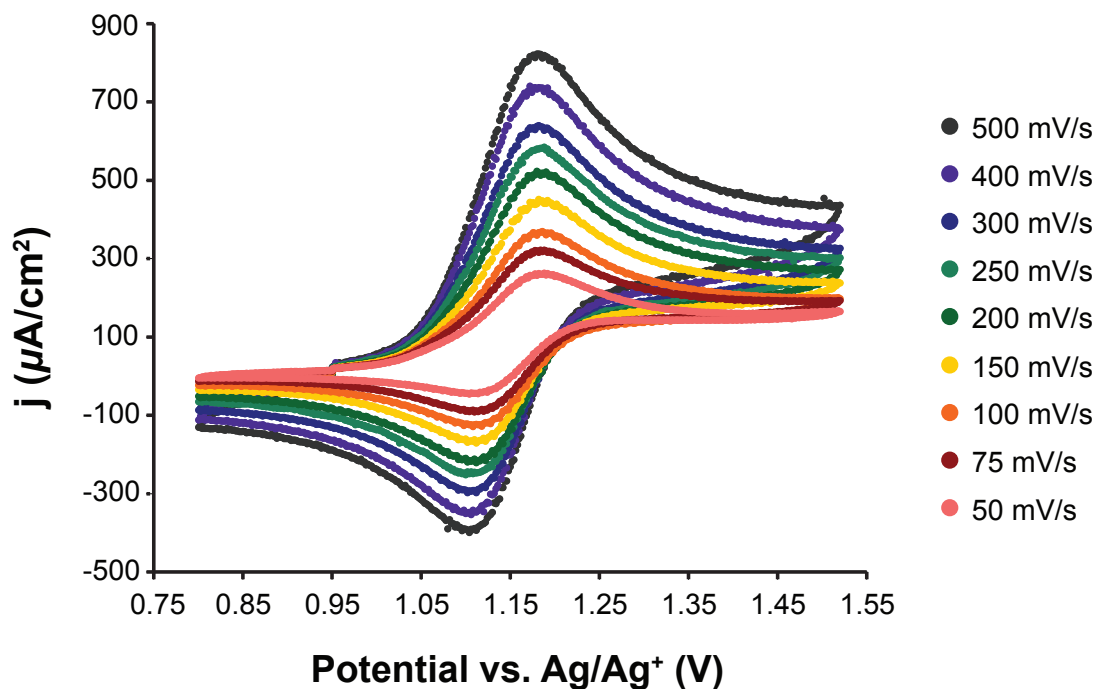


Figure 4.4. Variable scan rate cyclic votammagram of complex 3.2 (1 mM) in MeCN, 25 °C.

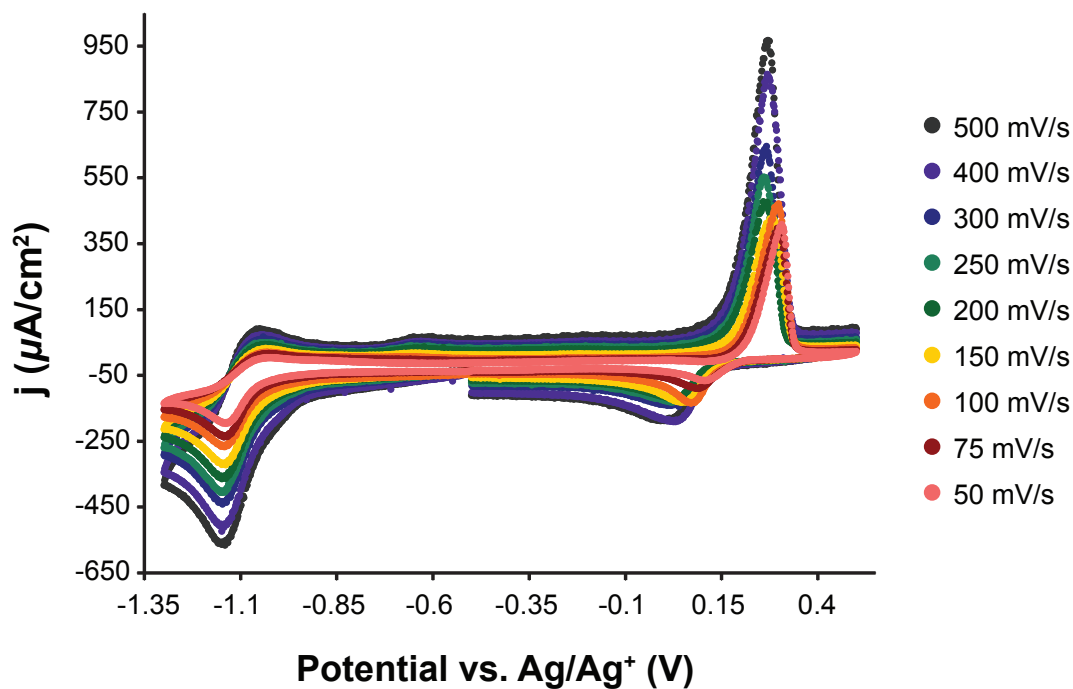


Figure 4.5. Variable scan rate cyclic votammagram of complex 3.3 (1 mM) in MeCN, 25 °C.

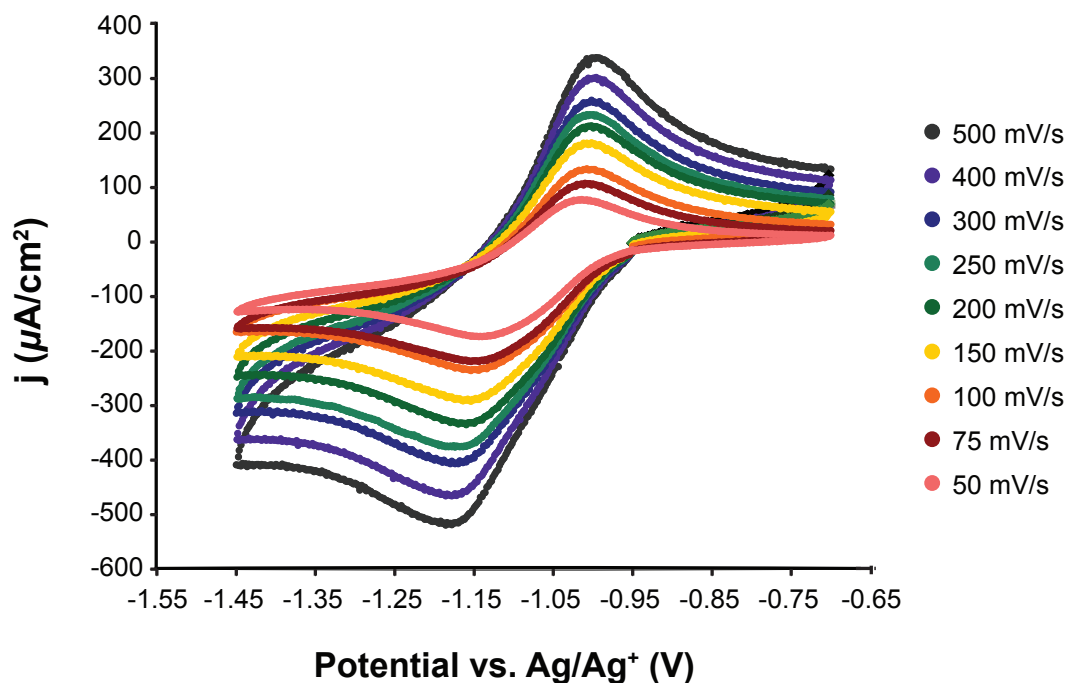


Figure 4.6. Variable scan rate cyclic voltammogram of complex **3.4** (1 mM) in MeCN, 25 °C.

Cobalt(II) is reduced to cobalt(I) but on the timescale of the CV experiment a disproportionation occurs to give both Co^0 and Co^{2+} , leaving no Co^{1+} in solution to be reoxidized back to Co^{2+} . The Co^0 is deposited as a black solid on the electrode surface. The adsorption-type oxidation peak seen around 300 mV is consistent with Co^0 being oxidized from the surface, and is absent if the potential is not initially swept in the reductive direction to the potential where the $\text{Co}^{2+}/\text{Co}^{1+}$ reduction occurs. At faster scan rates, some of the Co^{1+} is oxidized to Co^{2+} before disproportionation occurs, as is clearly seen by the growth in of an oxidation peak at -1.03 V (E_{pa} , Table 4.1).

The CV of nickel derivative **3.4** displays only one major redox event that is quasi-reversible (Figure 4.6). The half-wave potential of **3.4** has a value of -1.08 V ($E_{1/2}$, Table 4.1) and is assigned to a $\text{Ni}^{2+}/\text{Ni}^{1+}$ one-electron reduction. The peak-to-peak separation is too great to be considered a reversible process. This could possibly be due to the need for ligand exchange prior to reduction. From the solid-state structure presented in chapter 3, **3.4** is a 20-electron complex, and thus it seems logical that decoordination of a solvent molecule may be required before an electron can be added.

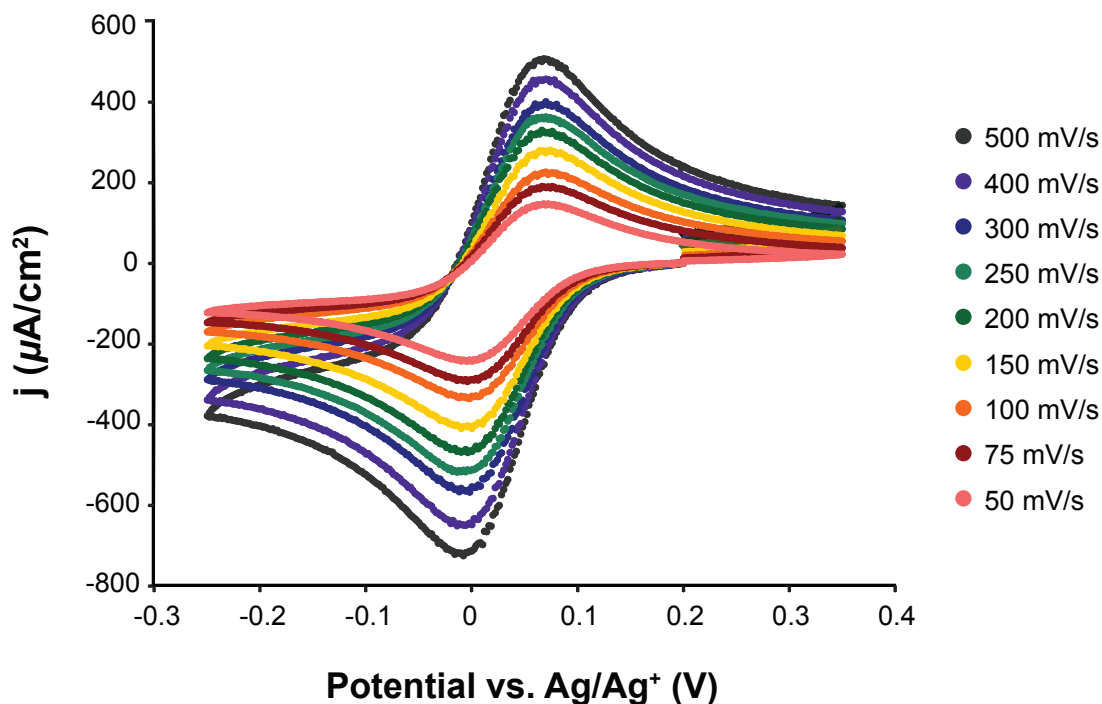


Figure 4.7. Variable scan rate cyclic voltammogram of complex **3.5** (1 mM) in MeCN, 25 °C.

Finally, the electrochemistry of copper complex **3.5** represents the other electrochemically reversible system of the series (Figure 4.7). Copper(II) complexes often display reversible $\text{Cu}^{2+}/\text{Cu}^{1+}$ redox couples. Complex **3.5** yields a redox potential of 0.03 V ($E_{1/2}$, Table 4.1) that corresponds to a reversible $\text{Cu}^{2+}/\text{Cu}^{1+}$ couple. This is comparable with other copper TPA dications reported in the literature, whose redox potentials reside around 0 V.^{45,46}

Complexes **3.2** and **3.5** display fully reversible redox couples, while the remainder of the series demonstrate quasi-reversible or irreversible behavior. However, upon bubbling oxygen into the electrochemical cell, the CVs of the manganese, iron, cobalt and copper derivatives changed dramatically. Dioxygen itself has a redox wave ($E_{1/2} = 0.85$ V) in MeCN assigned to the reversible one electron reduction to superoxide, providing a clear handle for observing any reactivity with the catalyst in solution.

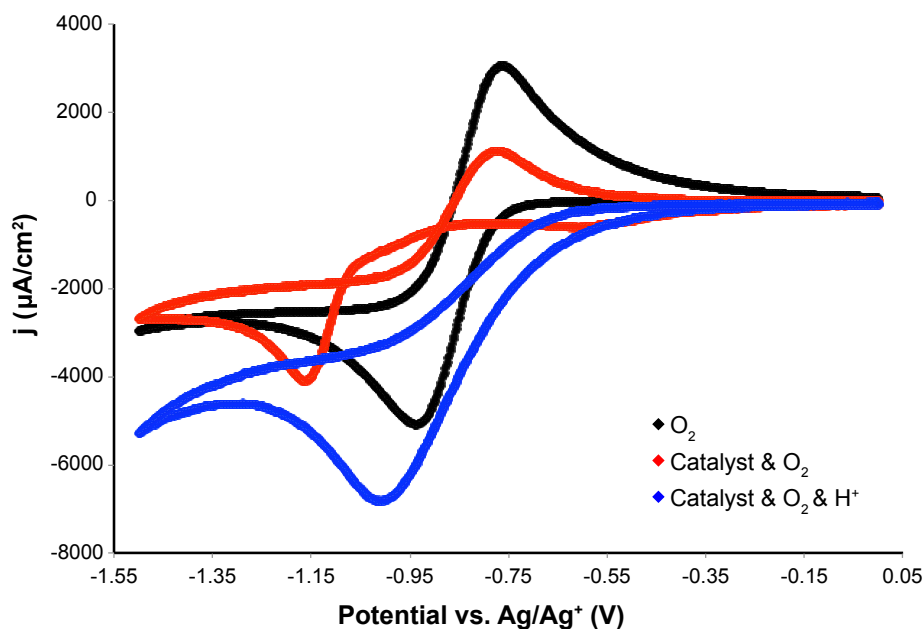


Figure 4.8. Cyclic voltammograms of complex **3.1** (1 mM) in the presence of 5 mM O_2 (red curve), and 5 mM O_2 and 0.1 M AcOH (blue curve) respectively, in MeCN at 25 °C. The cyclic voltammogram of O_2 in the absence of catalyst (black curve) is given for reference.

Cyclic Voltammetry in O_2 Saturated Solution. Upon introduction of complex **3.1** to an oxygen-saturated solution, the dioxygen redox wave becomes irreversible (Figure 4.8), indicating an interaction of the complex with the substrate. Subsequently, in order to mimic the protons that are conducted through the membrane to the cathode in a PEM fuel cell, acetic acid (AcOH) was added to the solution. In this instance, the redox wave is again irreversible, but the cathodic current occurs at an earlier onset potential (-0.36 V). Additionally, there is an increase in current density. Similar behavior is observed for complex **3.3** (Figure 4.10), with an even earlier onset potential (-0.31 V). These data indicate that **3.1** and **3.3** form oxygen adducts in solution and are able to facilitate reduction and subsequent protonation, giving an initial promising result as ORR catalysts.

Complex **3.2** also shows an interaction with dioxygen in the CV (Figure 4.9). As with **3.1** and **3.3**, upon addition of AcOH, there is an earlier onset potential of cathodic current (-0.31 V) and an increase in current density. However, upon examination of the free base TPA ligand under the same electrochemical conditions, an identical CV is observed. This indicates that two things are occurring in solution: first, protonation of the ligand is causing a decomposition of complex **3.2**, and second, the resulting free-base ligand is capable of facilitating oxygen reduction. While perhaps counterintuitive given that no metal center is present, similar behavior has been observed with free base porphyrins.⁴⁷ Complex **3.4** shows no interaction with dioxygen in the CV.

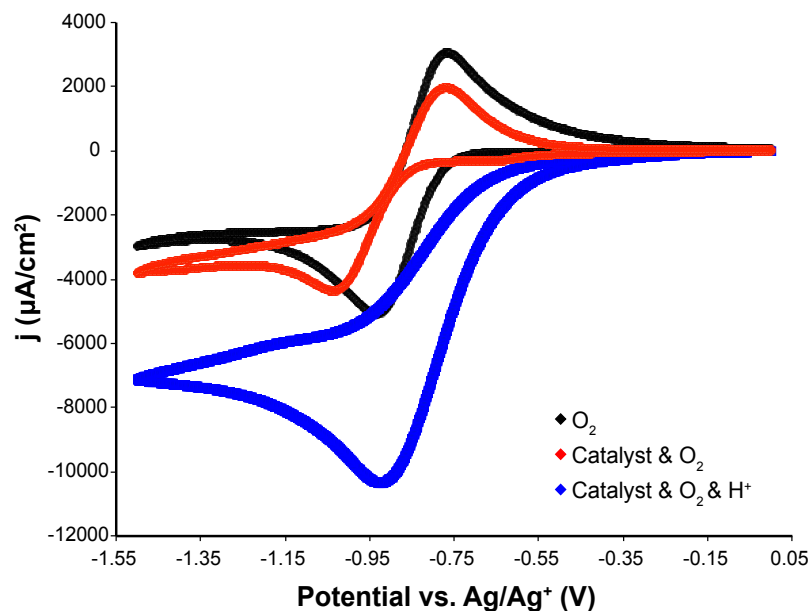


Figure 4.9. Cyclic voltammograms of complex **3.2** (1 mM) in the presence of 5 mM O_2 (red curve), and 5 mM O_2 and 0.1 M AcOH (blue curve) respectively, in MeCN at 25 °C. The cyclic voltammogram of O_2 in the absence of catalyst (black curve) is given for reference.

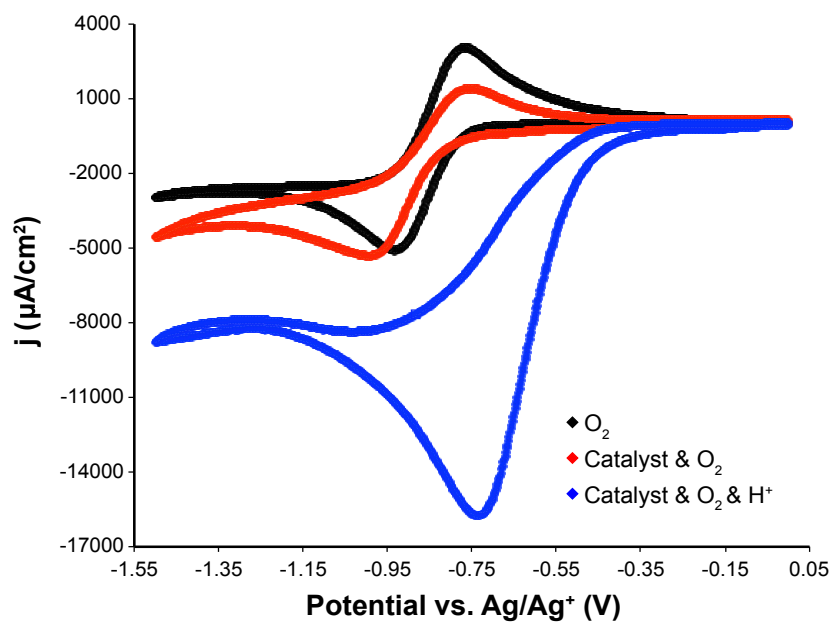


Figure 4.10. Cyclic voltammograms of complex **3.3** (1 mM) in the presence of 5 mM O_2 (red curve), and 5 mM O_2 and 0.1 M AcOH (blue curve) respectively, in MeCN at 25 °C. The cyclic voltammogram of O_2 in the absence of catalyst (black curve) is given for reference.

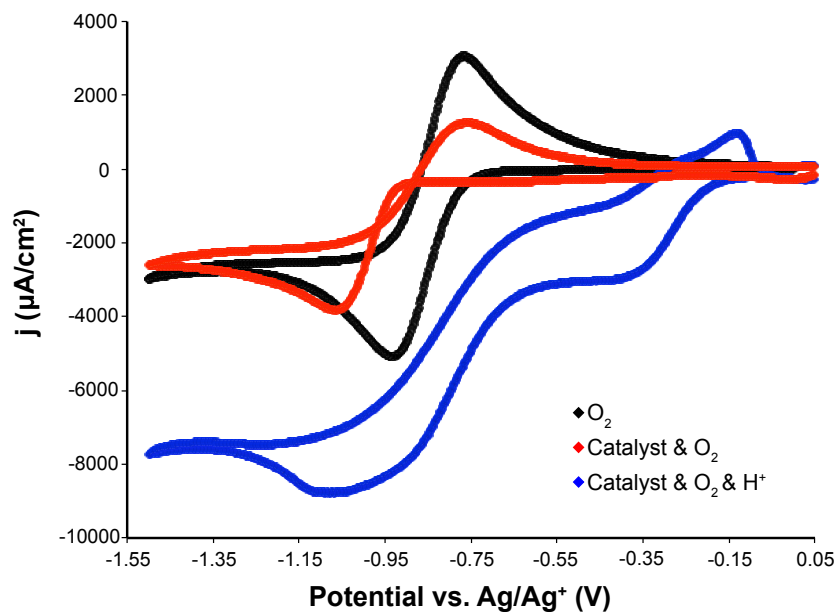
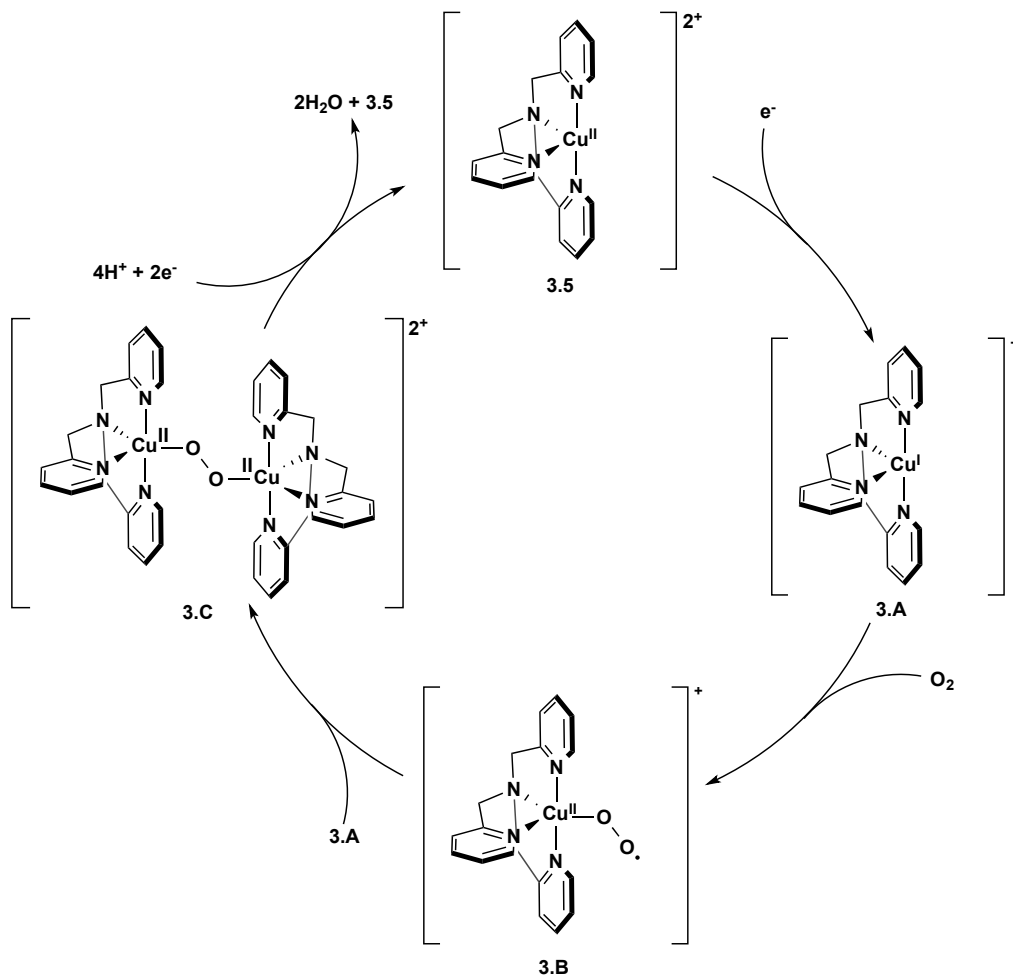


Figure 4.11. Cyclic voltammograms of complex **3.5** (1 mM) in the presence of 5 mM O_2 (red curve), and 5 mM O_2 and 0.1 M AcOH (blue curve) respectively, in MeCN at 25 °C. The cyclic voltammogram of O_2 in the absence of catalyst (black curve) is given for reference.

For copper complex **3.5**, again a loss of reversibility of the oxygen peak is observed. Likewise, upon addition of AcOH, both an earlier onset potential for cathodic current (-0.13 V) and an increase in current density are observed (Figure 4.11). However, in contrast to the singular waves that were observed for complexes **3.1** and **3.3** the wave for complex **3.5** shows two irreversible peaks. The mechanism of oxygen reduction for an analogous copper (II) TPA system that differs from **3.5** only in the counter anion present is well established in the literature and offers a reasonable explanation for the electrochemical behavior observed (Scheme 4.1).²⁵ First the copper(II) species is reduced to copper(I) (**3.A**), which is then able to react with dioxygen to give an end-on superoxo intermediate (**3.B**). Reaction of the superoxo species with an additional copper(II) center results in the formation of a μ -peroxo dimer (**3.C**), and subsequent reduction and protonation leads to regeneration of the catalyst and formation of H_2O_2 and/or H_2O as products. At the potentials relevant to this discussion, **3.5** is in its reduced copper(I) form, thus the reductive events observed are potentially the result of the reduction of the two oxygen adducts (**3.B** and **3.C**) presented in Scheme 4.1. The μ -peroxo species has a very characteristic visible band, therefore the use of spectroelectrochemical measurements would help to confirm the identity of the species observed in the CV of **3.5**.

Scheme 4.1. Proposed Electrocatalytic Mechanism for Oxygen Reduction by Copper Complex 3.5



Thin-Film Cyclic Voltammetry. Complexes **3.1–3.3** and **3.5** displayed reactivity towards oxygen in the solution-phase CV. As such, **3.1–3.3** and **3.5** were investigated employing a commonly used approach for studying ORR electrocatalysts. Each compound was adsorbed on aerogel carbon powder, made into an ink with Nafion and deposited on a glassy carbon disk/platinum ring electrode. Thin-film CVs were taken in acidic media (0.1 M HClO₄) under both inert and oxygen saturated atmospheres. Under these experimental conditions, which are necessary to test the fundamental properties of an oxygen-reduction electrocatalyst for fuel cells (0.1 M HClO₄), the initial redox state of complexes **3.1–3.3** and **3.5** is likely different from those seen in the solution-phase CVs presented above. However, when deposited on the surface, all four complexes were stable in aqueous acid for the length of the experiment, showing no degradation or loss of activity during electrochemical measurements. In deoxygenated solutions, the redox behavior of **3.1–3.3** and **3.5** is electrochemically irreversible. All show one redox couple associated with the complex, which are at lower overpotentials when compared to those measured in solution (E_{pc} , Table 4.2), suggesting, as predicted, that the coordination environment of complexes **3.1–3.3** and **3.5** after adsorption, is different from those observed in solution.

In the literature, the behavior of similar TPA complexes in the presence of water and acid has been well documented and, as mentioned previously, there is a body of knowledge regarding the metal-based redox states most often involved in oxygen reduction.^{48–51} These factors, in combination with the redox states observed in non-aqueous solution, and those described below for the complexes after surface deposition, make it likely that the complexes are operating as M^{3+}/M^{2+} (**3.1–3.3**) and M^{2+}/M^+ (**3.5**) redox couples.

According to the reductive event observed in the thin-film CV (E_{pc} , Table 4.2, Figure 4.12a), manganese complex **3.1** is reduced from manganese (III) to manganese (II). This is consistent with the fact that oxygen reduction chemistry observed with Mn catalysts employs the binding of oxygen to Mn(II) centers, followed by oxidation of the metal center and subsequent reduction, utilizing a III/II redox couple.⁵² These redox states correlate to those observed experimentally for **3.1** in non-aqueous conditions. Additionally of note is that given literature precedent for the formation of Mn(III) bis- μ -oxo TPA complexes upon reaction of similar species with water, a similar Mn(III) complex may exist in the film for **3.1**.⁴⁸

Similarly, iron complex **3.2** is reduced from iron (III) to iron (II) (E_{pc} , Table 4.2, Figure 4.12b). An Fe^{3+}/Fe^{2+} redox couple was observed in the non-aqueous CV, and using the same reasoning presented above, this redox couple is expected based on the oxygen reduction catalysis observed for iron compounds. Under the thin-film experimental conditions, the presence of either the μ -oxo dimer **3.6** presented in chapter 3 or a iron(III) diamond core dimer is expected.^{29,49}

The thin-film data for the cobalt complex **3.3** is more ambiguous (Figure 4.12c). While in the non-aqueous CV the redox couple observed was Co^{2+}/Co^{1+} , it is unlikely that this is the redox couple present in the thin-film CV. Based on a well-established understanding of the interaction of cobalt complexes with oxygen, as well as the established potential range for similar complexes, it seems that a Co^{3+}/Co^{2+} redox couple is much more probable.⁵³ In addition, there is literature precedent for the formation of a Co(III) bis- μ -hydroxo dimer under the

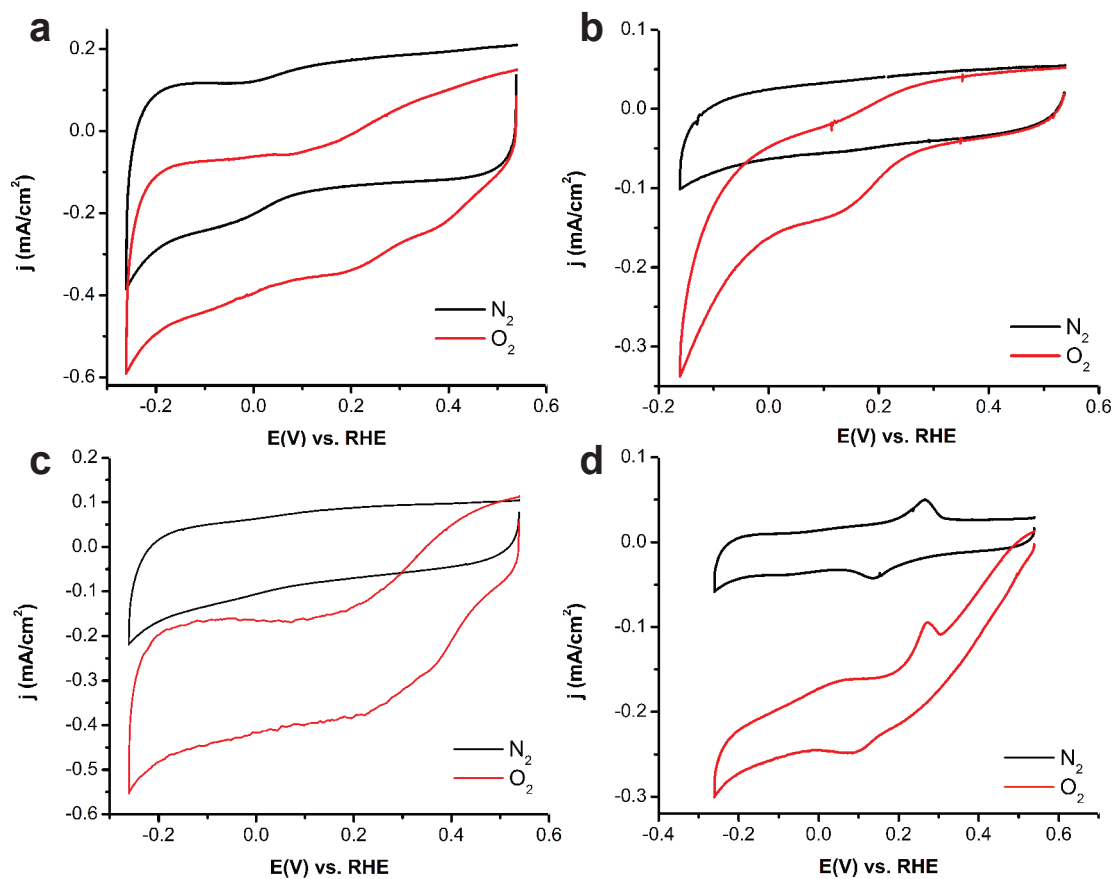


Figure 4.12. Cyclic voltammograms of complexes **3.1–3.3** and **3.5** (a–d, respectively) adsorbed on carbon in 0.1 M HClO₄ at 25 °C. Under inert atmosphere (black curve) and in an O₂ saturated solution (red curve).

Table 4.2. Electrochemical Data for Adsorbed Complexes **3.1–3.3** and **3.5**^a

Complex	E_{pc}^b	Catalytic O ₂ Reduction	
		$*E_{pc}^c$	% H ₂ O ₂ ^d
3.1	-0.02	+0.38, +0.23, -0.07	20
3.2	+0.15	+0.13	11
3.3	-0.02	+0.37, +0.26	28
3.5	+0.14	+0.27, +0.09, -0.07	0

^aMeasurements taken in 0.1 M HClO₄ at 25 °C. ^bCathodic peak potential under inert atmosphere (V vs. RHE). ^cCathodic peak potential in oxygen-saturated solution (V vs. RHE). ^dORR product yield (H₂O vs. H₂O₂) as calculated from the ring currents in Figure 4.13.

experimental conditions used, which is consistent with the reduction wave that is observed first in the thin-film CV (E_{pc} , Table 4.2).⁵⁰

Consistent with the redox behavior seen in the non-aqueous electrochemistry, complex **3.5** exhibits a reduction peak assigned to a Cu²⁺/Cu¹⁺ couple (E_{pc} , Table 4, Figure 4.12d). This is similar to the oxygen reduction chemistry observed for the analogous TPA system mentioned previously, in which Cu²⁺ is first reduced, followed by a reaction with oxygen.²⁵ Additionally, this behavior suggests that, unlike the previous three complexes studied, **3.5** is not altered under the experimental conditions of RRDE. In general, under the relatively harsh conditions utilized above, a change in the redox state of the metal complex from that observed in organic solvents, as is seen with **3.1–3.3**, is expected and has been observed with various molecular catalysts.^{51,54}

Thin-Film Cyclic Voltammetry in O₂ Saturated Solution. Subsequently, in order to determine the ORR activity of complexes **3.1–3.3** and **3.5** after adsorption, thin-film cyclic voltammograms were taken in the presence of oxygen. The curves display a significant increase in current density when compared to those conducted under inert atmosphere (Figure 4.12, red waves). This is attributed to catalytic oxygen reduction activity by the complexes, as the aerogel carbon has no ORR activity in this potential range.⁵⁵ Oxygen reduction occurs at multiple potentials for complexes **3.1**, **3.3** and **3.5**, with each complex exhibiting multiple cathodic peaks ($*E_{pc}$, Table 4.2). For each of the four complexes, the $*E_{pc}$ with the lowest overpotential where oxygen reduction is observed lacks an associated oxidation peak. These observations are consistent with the reduction of the metal center, followed by subsequent electron transfer to an oxygen adduct of complexes **3.1–3.3** and **3.5**, reducing oxygen either via a two-electron reduction to peroxide, or a four-electron reduction to water. The catalyst is chemically regenerated by reaction with oxygen and thus, an anodic wave is not observed. Interestingly, the oxygen reduction onset potential, which is approximately 0.44 V for all complexes in the series investigated (Figure 4.13), does not seem to be drastically affected by the metal center present. This may indicate that the ligand has more of an affect over the potential where ORR occurs, as was also observed

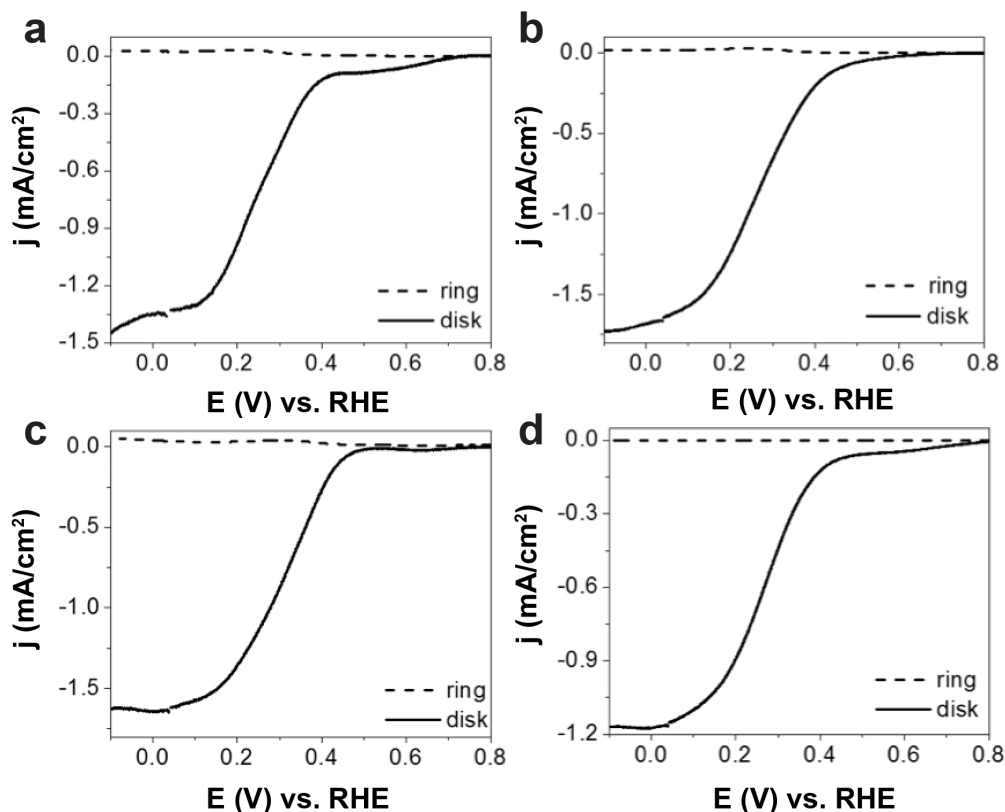


Figure 4.13. RRDE voltammograms for **3.1–3.3** and **3.5** (a-d respectively) in oxygen saturated 0.1 M HClO₄ at 1 mV/s and 400 rpm.

with metalloporphyrins, which show dependence of redox potential on the substituents on the ligand as a result of their electron withdrawing or donating properties.⁵⁶ However, this could also potentially be due to a kinetic limitation of the system, given the stark thermodynamic potential differences observed for **3.1–3.3** and **3.5** in solution (Figures 4.3–4.5 and 4.7).

Rotating Ring-Disk Voltammetry. Additionally, the propensity for two versus four-electron oxygen reduction, as catalyzed by **3.1–3.3** and **3.5**, was studied using rotating ring-disk electrode (RRDE) voltammetry. The RRDE voltammograms for complexes **3.1–3.3** and **3.5** (Figure 4.13) all display several disk waves. Although the onset potentials for oxygen reduction do not vary appreciably for **3.1–3.3** and **3.5**, the product yields (H₂O vs. H₂O₂) appear to be significantly affected by the metal center present (Table 4.2). While all four complexes display excellent selectivity for four-electron reduction, with **3.1–3.3** demonstrating 80, 89 and 72% conversion respectively, the copper complex **3.5** exhibits complete conversion to water.

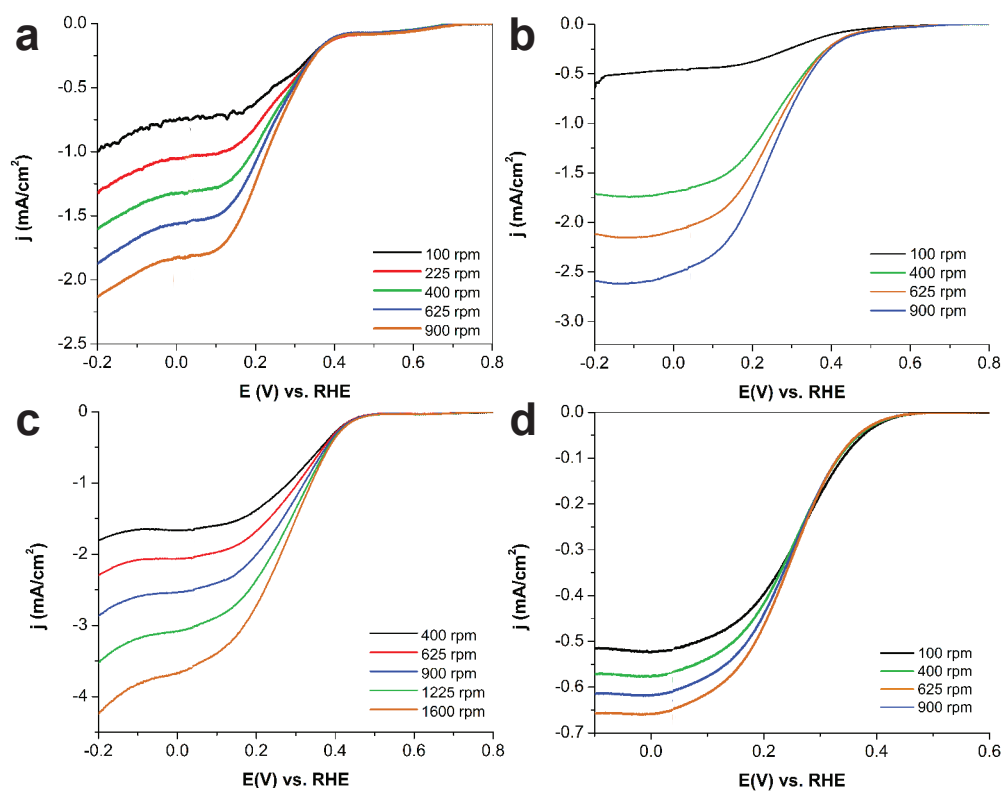


Figure 4.14. Rotating disk voltammograms of complexes **3.1–3.3** and **3.5** (a-d, respectively) adsorbed on carbon at variable rotation rates in an O_2 saturated solution and 0.1 M HClO_4 at 25 °C.

Rotating Disk Voltammetry. Finally, in order to determine the kinetic proficiencies of **3.1–3.3** and **3.5**, rotating disk voltammograms were taken (Figure 4.14). Applying linear regression analysis to the data, the limiting current at infinite rotation speeds can be extrapolated from the y-intercept to construct Koutecky-Levich plots (Figure 4.15).⁵⁷ The kinetic currents for **3.1–3.3** and **3.5** are 0.5, 7.6, 0.5 and 1.5 mA respectively, and are directly related to the heterogeneous rate constant for oxygen reduction. As with the onset potential for oxygen reduction, as well as the peroxide yield, the kinetics of **3.1–3.3** and **3.5** are comparable to those obtained under similar conditions for molecular species that have been employed as fuel cell catalysts.⁵⁸ While the oxygen reduction potential does not shift significantly between the complexes examined, as with the propensity for four-electron reduction, the kinetic efficiency of the catalyst does change with the metal center, with the iron complex **3.2** being the most kinetically active of the series. Given the great deal of literature precedent concerning the mechanisms employed by various oxygen reduction catalysts, it is likely that the differences in ORR performance observed for **3.1–3.3** and **3.5** are linked both to the ability of each catalyst to employ bimetallic cooperativity and their mode of dioxygen binding. However, further electrochemical and characterization studies are necessary before direct structure function relationships can be definitively asserted.

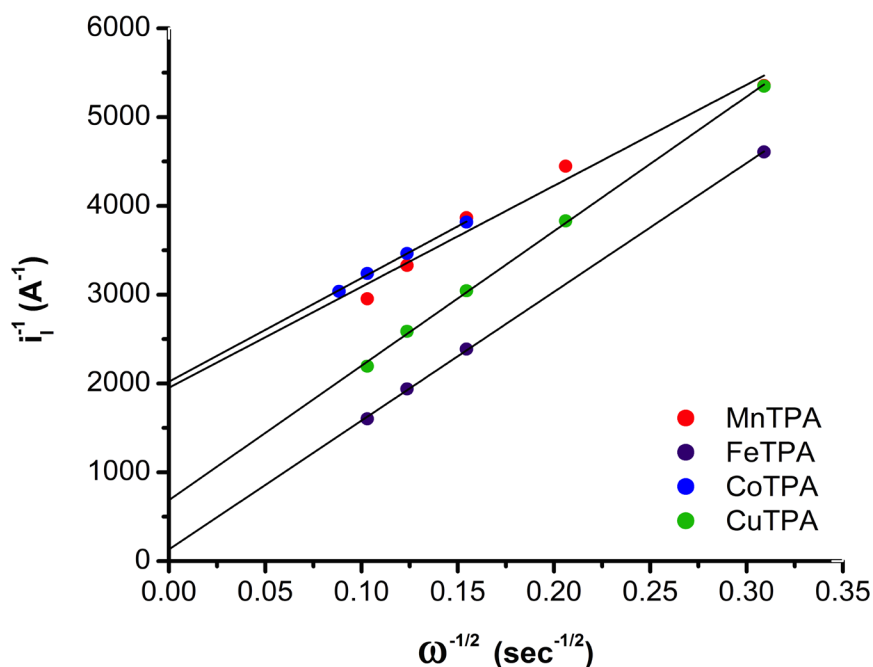


Figure 4.15. Koutecky-Levich plots of complexes 3.1–3.3 and 3.5.

Conclusions

A series of simple first row transition metal complexes $[(TPA)M^{2+}]^{n+}$ ($M = Mn, Fe, Co, Ni$ and Cu) have been examined as oxygen reduction catalysts for fuel cell applications. Compounds 3.1, 3.2, 3.3 and 3.5 were shown to electrocatalytically reduce dioxygen to water in a selective manner. All complexes showed onset potentials for ORR of roughly 0.44 V vs. RHE, and displayed excellent selectivity for four-electron reduction over two-electron reduction ($<28\%$ H_2O_2), crucial for fuel cell applications. Complex 3.5 demonstrates complete conversion to H_2O . Additionally, the kinetic currents demonstrated by the complexes vary from 0.5–7.6 mA respectively, with the iron complex 3.2 being the most active. These electrocatalytic properties are comparable to, and in some instances better than, current molecular catalysts in the literature. For the series presented, the metal center appears to dictate the peroxide yield and thus reaction kinetics, whereas the overpotential required to reduce oxygen seems to be influenced more strongly by the ligand.

Experimental Details

General Procedures. Unless otherwise noted, all procedures were conducted using standard Schlenk line techniques or in an MBraun N₂-atmosphere glovebox (< 1 ppm O₂/H₂O). All glassware was stored in an oven at ca. 150 °C. Acetonitrile was distilled from P₂O₅ and degassed prior to use. Complexes **3.1–3.5** were prepared according to the procedures reported in chapter 3. The remaining starting materials were obtained from commercial sources and used without further purification.

Electrochemical Procedures. Solution cyclic voltammograms were recorded with a Gamry Reference 600 potentiostat, using a glassy carbon working electrode (0.07 cm²), a 'no leak' silver/silver ion (Ag/AgNO₃) reference electrode calibrated to the ferrocinium/ferrocene redox couple (at 0.00 V), and a platinum counter electrode. Acetonitrile was used as the solvent with 0.1 M (nBu₄N)(PF₆) as supporting electrolyte. All solutions examined by CV were purged with nitrogen. ORR electrochemical measurements were conducted using a Princeton Applied Research (PAR) VMP3 multi-potentiostat and a Pine Instruments rotator. Two milligrams of complexes **3.1–3.3** and **3.5** were dissolved in 1 ml of water (18 MΩ•cm Millipore) combined with 1 cm² of aerogel carbon paper (Marketch International, Inc.), and allowed to adsorb on the carbon support for 24 h. The samples were then ground into a fine powder using a mortar and pestle. The powder was dissolved in 1 ml of DI water and sonicated for 30 min. Nafion (200 μL, 5% solution) was added to the catalyst ink and left to adsorb for 4 h. The ink (20 μL) was deposited on a glassy carbon disk (0.2475 cm²) and allowed to air-dry. All experiments were conducted in 0.1 M HClO₄ using a rotating platinum ring—glassy carbon disk electrode (RRDE), a reversible hydrogen (RHE) reference electrode at 25 °C and a glassy carbon counter electrode. Thin-film cyclic voltammograms were conducted first under an inert atmosphere and subsequently in oxygen-saturated solutions. RRDE experiments in oxygen-saturated solutions were conducted at a scan rate of 1 mV/s in order to minimize the columbic currents from the high surface area carbon support.

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Chapter 4

(57) Koutecky-Levich plots (Figure 4.15) were constructed from the rotating disk voltammogram data (Figure 4.14) according to the following equation:

$$1/iL = 1/i_{\text{Lev}} + 1/i_k$$

where i_{Lev} is the Levich current given by:

$$i_{\text{Lev}} = 0.62nFAD^{2/3}\omega^{1/2}\nu^{-1/6}C_{\text{O}_2}^*$$

and i_k is the kinetic current defined by:

$$i_k = nFAk\Gamma C_{\text{O}_2}^*$$

where A is the electrode area cm^2 , D and C are the oxygen diffusion coefficient $\text{cm}^2 \text{s}^{-1}$ and bulk concentration mol L^{-1} , respectively, ν is the kinematic viscosity of the solution $\text{cm}^2 \text{s}^{-1}$, ω is the angular frequency of rotation ($\omega = 2\pi f/60$, f is the disk rotation rate rpm), k is the rate constant $\text{M}^{-1} \text{s}^{-1}$ governing the reaction of the catalyst with oxygen, and Γ is the surface coverage mol cm^{-2} of the catalyst.

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Future Directions

Future Directions

Overview

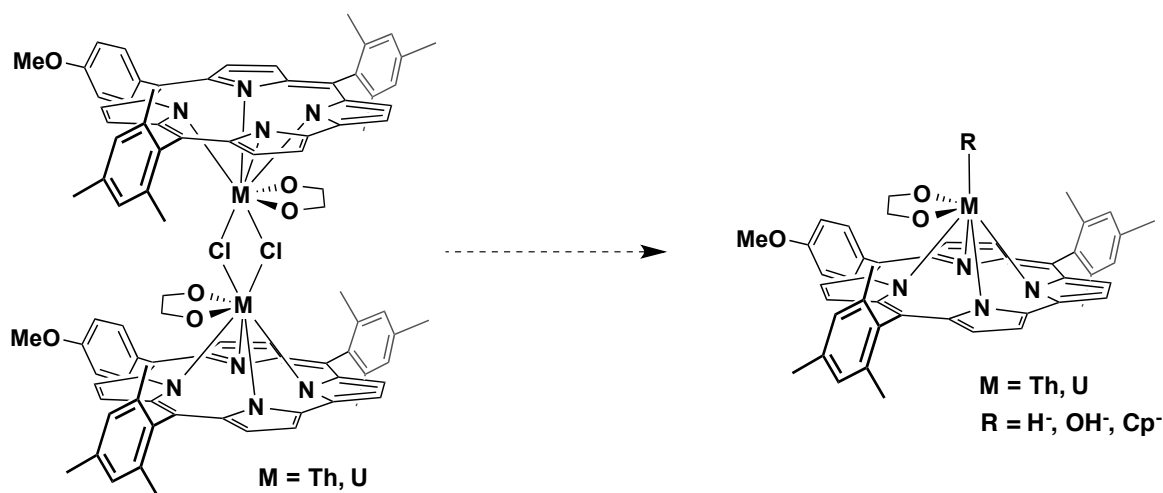
While the actinide–transition metal bonded complexes presented in chapter 1 and the actinide corrole system presented in chapter 2 have been characterized in great detail, and preliminary reactivity was presented, there remains a great deal of chemistry to be explored. The viability of the actinide N_4P_3 and corrole systems as rich starting platforms for actinide bonding and reactivity has yet to be expanded upon. The focus of this chapter will be to highlight promising areas of study for both systems.

Actinide Corrole Complexes

Synthesis. The electrochemistry that was carried out on the actinide corrole complexes and presented in chapter 2 indicates that there are two readily accessible oxidations for both **2.1** (Figure 2.9) and **2.2** (Figure 2.10). Stepwise chemical oxidations of both **2.1** and **2.2** would help to confirm the nature of these electrochemical oxidations. In the cyclic voltammograms the oxidations are one electron processes and, based on the similarity in potentials between **2.1** and **2.2**, are likely ligand based. Isolation and characterization of these oxidation products would identify whether an electron was removed from the metal center or the ligand. The reactivity of these higher valent complexes should vary from those of the starting material and would be interesting in that respect as well.

Additionally, the cyclic voltammograms of **2.1** (Figure 2.9) and **2.2** (Figure 2.10) show an irreversible reduction at negative potentials (~ -1.8 V vs. SHE). While these reductions are electrochemically irreversible, the reduction products may be accessible via chemical reduction.

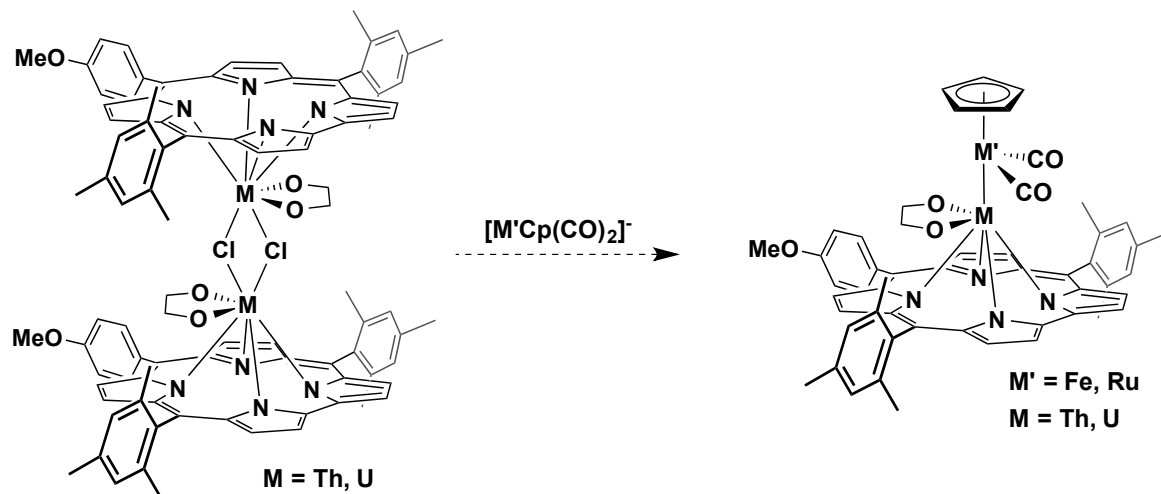
Scheme FD.1. Proposed Synthesis of Thorium(IV) Corrole **2.1** and Uranium(IV) Corrole **2.2** Substitution Products^a



^aMethyl groups of coordinated DME molecules have been omitted for clarity.

Future Directions

Scheme FD.2. Proposed Synthesis of Metal–Metal Bonded Complexes of Thorium(IV) Corrole **2.1** and Uranium(IV) Corrole **2.2**^a



^aMethyl groups of coordinated DME molecules have been omitted for clarity.

Based on the similarity in reduction potential and the known potentials for the reduction of thorium (IV) and uranium (IV), this reduction, as with the oxidations, is likely ligand based. However, these types of complexes would be of interest from an electronic structure standpoint and would lend credit to the ability of corroles to act as redox active ligands capable of stabilizing highly reactive metal centers in a variety of oxidation states. Accessing a reduced species of complex **2.1** would be interesting electronically, as detailed spectroscopic characterization should reveal if the complex is formally thorium (III) or if the electron resides in the ligand backbone. Additionally, the chemistry of similar porphyrin complexes involving halide bridged dimers has led to the formation of metal–metal bonds upon reduction. Compounds of this nature for actinides are highly sought after.

In addition to redox chemistry, substitution chemistry is also readily available for **2.1** and **2.2**. Establishing the viability of the actinide corrole complexes as a platform for future chemistry depends on first achieving simple reactivity. As such, reactions to exchange the chloride for other ligands is desirable. Substitutions for ligands such as hydrides, hydroxides or cyclopentadienyl derivatives could be a straightforward starting point. Chemistry of this kind is illustrated in Scheme FD.1.

Lastly, the actinide corrole complexes serve as a suitable starting point to target metal–metal bonds. One face of the molecule is protected sterically by the corrole ring itself and the other face is distorted away from the plane of the corrole and has a moiety capable of substitution. Initially, salt metathesis with the chloride ligands should be attempted. A variety of transition metal anions suitable for this purpose exist and would be straightforward to screen. Perhaps the most suitable reagents for this task would be the $[M(\text{Cp})(\text{CO})_2]^-$ anions (Scheme FD.2), which have proven to be useful precursors for forming metal–metal bonds and would offer additional steric protection along the other side of the molecule.

Future Directions

Characterization. Having a thorium analogue to the uranium corrole offers a convenient diamagnetic handle for determining the success of any future chemistry. As such, new thorium complexes should be targeted first and then characterized in a straightforward manner by ^1H NMR. Given the extent to which thorium and uranium chemistry are orthogonal, establishing a synthetic route to a new thorium compound should be transferable to the uranium analogue. UV–visible spectroscopy will be useful as an initial characterization method as well, given that each corrole complex has unique Soret and Q bands, indicative of how the corrole ring distorts as a function of metal center binding.

X-ray crystallography will provide important solid-state characterization data. Not only will such data be essential in confirming the structure of uranium analogues, but more generally this information will help to elucidate the nature of the reduction and oxidation products in both thorium and uranium complexes, as telling structural changes in the ligand backbone occur if the electron transfer process is ligand centered. Additionally, metal–metal bonds in actinide chemistry remain quite rare as compared with the rest of the periodic table. Therefore, any new solid-state data that is obtained on any resulting metal–metal bonds will help to add to a very limited knowledge base.

For the metal–metal bonded compounds, further characterization using electrochemical techniques may provide new information on the nature of redox events influenced by the presence of another metal center. Additionally, X-ray Absorption Near-Edge Spectroscopy (XANES) measurements, coupled with theoretical work (*see below*), will help to determine the nature of the unprecedented bonding in these complexes.

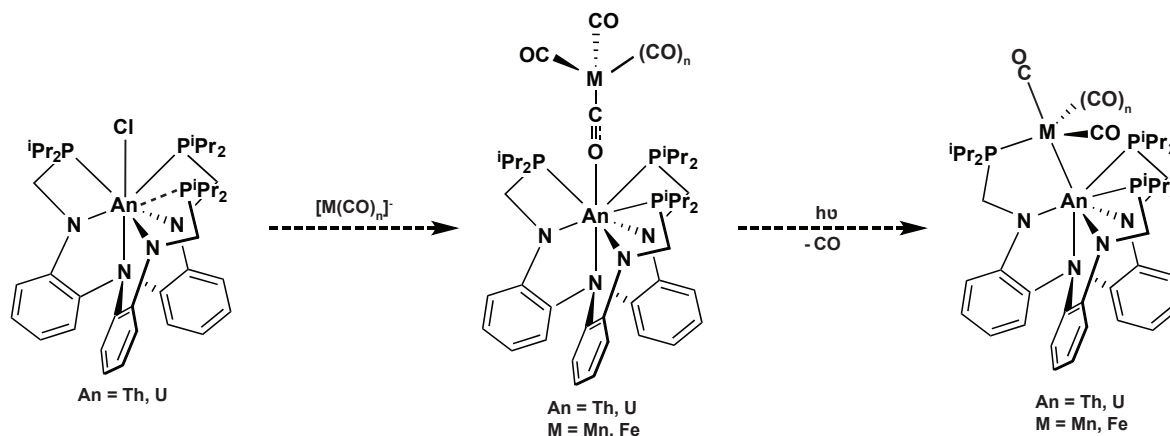
Theory. Theoretical work on this series of complexes should initially involve DFT calculations of **2.1** and **2.2** as a baseline for any future studies. Additionally, calculations of the thorium and uranium corrole complexes are essential for definitively assigning the UV–vis spectra presented in chapter 2 and could also help to assign the electrochemical processes observed in the cyclic voltammograms. Once calculations that are in good agreement with experimental data for complexes **2.1** and **2.2** are reached, theoretical work to determine the nature of the electronics of any resulting metal–metal bonds can be done. As mentioned above, theory will also be key to interpreting XANES data.

Actinide N_4P_3 Complexes

Synthesis. An important first step in furthering the chemistry of the N_4P_3 system is to determine if further photolysis of complexes **1.6** and **1.7** is possible. Under the reaction conditions described in chapter 1, it seems that photolysis ceases after the bridging carbonyl is removed. It is possible that due to the much larger size of the actinides, and their resulting distortion above the nitrogen coordination plane of the ligand, that further photolysis is limited due to steric constraints. However, the reaction was carried out in toluene which is a strong UV absorber and could potentially prevent photolysis of subsequent carbonyl ligands. Additionally, the main group and transition metal examples of metal–metal bonded complexes of this ligand fully coordinate all phosphine ligands to the secondary metal center. Hence, it may be possible to carry out further photolysis in a stepwise fashion, in which case it would be interesting to observe the effect of ligand substitution on the metal–metal bond.

Future Directions

Scheme FD.3. Proposed Synthesis of New Metal–Metal Bonded Derivatives of Thorium and Uranium N_4P_3 Complexes **1.1** and **1.2**



Another area of exploration for complexes **1.6** and **1.7** is to investigate the reactivity of the metal–metal bond. Reaction with small molecules would be of particular interest, as transition metal and main group heterobimetallics have been investigated for this purpose. Additionally, there are many examples of actinide complexes exhibiting small molecule activation and often the mechanism of this reactivity is different from that their transition metal counterparts. Utilizing an actinide–transition metal heterobimetallic for small molecule activation grants the opportunity to exploit unique *f*-element properties in combination with bimetallic cooperativity. Reasonable small molecules to initially explore reactivity of the heterobimetallics with include CO_2 , CO , H_2 , ethylene, N_2O , O_2 and amines.

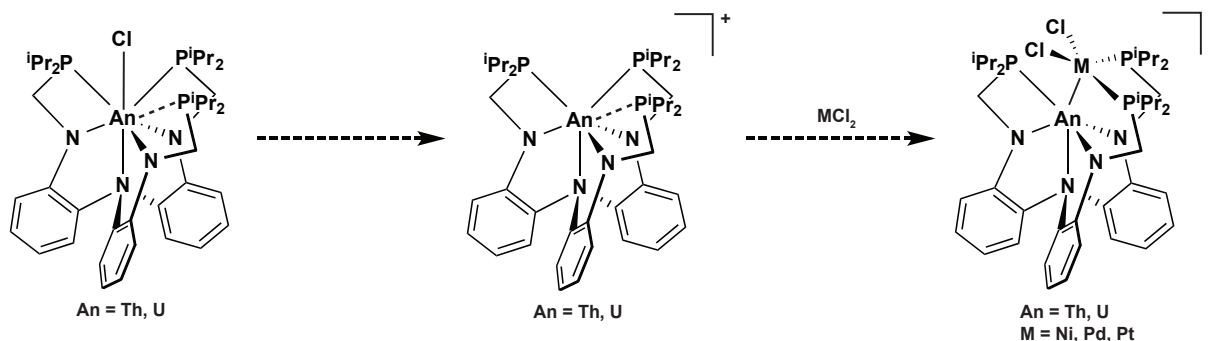
Perhaps the most obvious chemistry to explore with complexes **1.2** and **1.3** is to develop a series of first row transition metal–actinide heterobimetallics. Anionic metal carbonyl complexes of manganese $[Mn(CO)_5]^-$ and iron $[Fe(CO)_4]^{2-}$ are readily synthetically accessible and salt metathesis reactions between these species and the actinide N_4P_3 chlorides **1.2** and **1.3** should give isocarbonyls analogous to **1.4** and **1.5** (Scheme FD.3). Investigating the bonding properties across the first row would be an interesting study. Additionally, the $[M(Cp)(CO)_n]^-$ anions are available and there is literature precedent for the binding of such moieties to actinide centers. This would offer a more protected metal–metal bond and should have different properties.

Exchange of the chloride ligand in complexes **1.2** and **1.3** is essential for facilitating further reactivity. However, an alternative way to create an open coordination site at the actinide center would be to target cationic complexes of **1.2** and **1.3** (Scheme FD.4). Synthesis of actinide complexes with outer sphere anions would allow for the targeting of metal–metal bonds facilitated via methods alternative to salt metathesis. The phosphine ligands could instead be used to coordinate neutral metals in the upper coordination sphere and the metal–metal bond could be achieved via a drive to relieve the coordinative unsaturation of the cationic actinide center.

The electrochemistry of the series of complexes presented in chapter 1 remains to be explored (*see below*). However, regardless of these results, chemical reductions and oxidations

Future Directions

Scheme FD.4. Proposed Synthesis of Cationic Derivatives of Thorium and Uranium N_4P_3 Complexes **1.1** and **1.2**



of complexes **1.2** and **1.3** should be targeted. Attempts to access a uranium(III) complex of the N_4P_3 ligand via uranium(III) starting materials were unsuccessful due to disproportionation reactions. However, this type of reactivity is not unprecedented and U(III) complexes are often accessed through chemical reduction of their U(IV) analogues. Additionally, oxidation of the U(IV) complex **1.2** in a stepwise fashion could grant access to U(V) and U(VI) complexes. The reactivity of the actinides differs greatly as a function of oxidation state, and accessing these derivatives and testing subsequent reactivity via the same ligand platform would be useful.

There is potential to use the N_4P_3 ligand platform to facilitate an actinide–actinide bond: the holy grail of *f*-element chemistry. Reaction of the starting complexes **1.2** and **1.3** with other actinide starting materials may result in bridged halide complexes. Their subsequent reduction may result in loss of halogens and formation of metal–metal bonds. Additionally, reaction of the cations and reduced derivatives mentioned above with various actinide starting materials may also provide a way to target actinide–actinide bonds with this system.

Finally, an additional way forward with this ligand system is to vary the ligand itself. There are three major areas for such modifications. The first is in the ligand backbone. Increasing the size of the lower binding pocket may alleviate some of the steric issues associated with the larger size of the actinide ions bound in the lower coordination sphere. A straightforward way to do this would be to synthesize a derivative with an alkyl linker between the basal nitrogen and the aryl arms of the ligand, making the lower binding pocket larger. The next option for ligand modification is to change the substituents on the phosphines. A derivative of the ligand with phenyl groups in place of isopropyls has been synthesized in our lab, but it is simple to envision many additional alternatives. The final ligand alteration is accessed through reaction of the phosphines themselves. Ligand derivatives such as phosphinimines, phosphine sulfides and phosphine oxides would greatly alter both the electronics and the sterics of the N_4P_3 ligand (Figure FD.1). The binding pocket for the upper coordination sphere would be larger with each of these derivatives as it incorporates an additional atom into the ligand arm. Additionally, incorporation of harder donors such as nitrogen and oxygen could allow for early transition metals, lanthanides or actinides to be incorporated into the secondary coordination sphere.

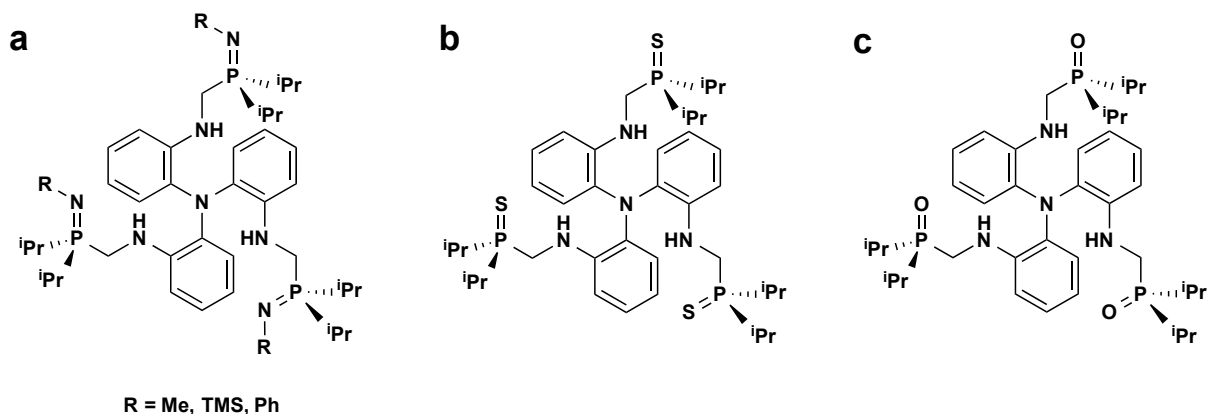


Figure FD.1. a) Various phosphinimine derivatives of the N_4P_3 ligand. b) Phosphine sulfide ligand derivative. c) Phosphine oxide ligand derivative.

Characterization. Electrochemical characterization has yet to be conducted on the existing N_4P_3 complexes. Cyclic voltammetry in particular will be useful for determining the accessibility of any reduction or oxidation products of **1.2** and **1.3** as discussed above. The thorium complex offers a redox silent point of reference, as redox behavior should not be observed within a standard CV window for thorium (IV). Subsequently, any electrochemical reactivity observed upon binding of a secondary metal can be attributed to that metal alone. This will serve as a useful point of comparison for the analogous uranium system, which could show redox activity within a standard CV range. Hence, the nature of any electrochemical behavior observed for the heterobimetallics can be deconvoluted.

As with the actinide corrole complexes, the fact that a thorium analogue is readily available and is straightforward to characterize by NMR makes it a good starting point for testing new reactivity. Thorium complexes of the aforementioned derivatives will be targeted first, and, particularly with the ^{31}P NMR handle of the ligand, reactions can be easily screened for success on a very small scale. Any successful synthetic routes can then be carried over to the uranium system. X-ray crystallography studies will be needed to confirm the identity of any uranium species synthesized. These studies will also be carried out on any new thorium complexes, as structural information will be key to characterizing any new metal–metal bonds formed.

The carbonyl ligands present in the majority of complexes highlighted above offer a convenient spectroscopic handle. Infrared studies should be carried out on any carbonyl containing derivatives and the results can be used as a probe of the electronics of the metal–metal bond. UV–vis/NIR studies will also be conducted, and with the assistance of DFT calculations (*see below*), the nature of any resulting transitions can be assigned. Of particular interest are the NIR bands (Figure 1.11), which appear to correlate with the metal–metal bond. Finally, XANES measurements should be conducted to gather structural and bonding information in conjunction with theory.

Future Directions

Theory. Theoretical calculations will be imperative to assigning much of the characterization data described above. DFT calculations will help to assign electrochemical events, UV–vis/NIR transitions and XANES spectra. Additionally, coupled with X-ray structural data, theory can help to determine the properties of any new metal–metal bonds formed.