ABSTRACT

HUANG, TAO. Synthesis, Structure, Magnetic and Electronic Properties of Heterometallic Complexes Containing First-Row Transition Metals. (Under the direction of Walter W. Weare.)

Heterobimetallic complexes can be used as molecular analogues for complicated polymetallic systems. Explorations of such molecular systems can provide essential understanding that enables the rational design of molecular based electronic devices and metal-to-metal charge transfer chromophore for artificial photosynthetic systems. One of the major questions about metal-metal interactions in such systems is related to spin-spin exchange interactions in both the ground and excited state. We have designed a series of oxido-bridged heterometallic complexes in order to begin a deeper understanding of such spin-spin exchange interactions.

In Chapter 1, I discuss Anderson's and Kahn's models that examine spin-spin interactions. Using their approach, I demonstrate that such interactions are controlled by a kinetic exchange pathway through mixing charge delocalization character or charge transfer excited state into the ground state for these oxido-bridged complexes.

In Chapter 2, the synthesis of heterometallic complexes containing chromium (III) and titanium (IV) is described. With twelve Cr–O–Ti bi/trimetallic complexes being electrochemically and structurally characterized, we have shown that strictly controlling reaction stoichiometry is necessary to obtain such species. The structural and electrochemical properties are also discussed.

In Chapter 3, we extend our synthetic approach to obtain d^{3}d^{1} Cr–O–V bi/trimetallic complexes. The magnetic interactions between the metal centers was explored, showing the first examples of ferromagnetically coupled oxido-bridged complexes. This was determined to
be due to the linear bridging geometry of the oxido-bridge, which promotes ferromagnetic superexchange interactions through π orbitals and confirms a long-standing theoretical prediction for such a linkage.

In Chapter 4, we further explore such exchange interactions that are based on the kinetic exchange model. The exchange integral (the overlap between magnetic orbitals) between two paramagnetic centers is found to be important to generate effective ferromagnetic coupling. We identify a molecular twist of (omtaa)V=O molecule that can be used to tune the magnitude of ferromagnetic coupling, resulting in a significant change of J values in otherwise structurally similar complexes (~+3 cm\(^{-1}\) to ~+40 cm\(^{-1}\)).

In Chapter 5, we introduce a new synthetic approach to achieve phenoxido-bridged heterometallic complexes that exhibit a bent geometry around the bridge. An antiferromagnetic coupling, which can be explained utilizing our previously described model, was identified. This is in contrast with the ferromagnetic coupling of the same electronic configuration for a linear complex. This work has confirmed that controlling bridging geometry can be used to switch the sign of magnetic coupling for such early transition metal systems.

In Chapter 6, we summarize the magnetic coupling of all known oxido-bridged heterometallic complexes with first-row transition metals. The resulting data is used to generate a re-parametrization of the kinetic exchange model using linear regression. This results in two major transfer integrals based on σ and π orbitals. This result can be used to reproduce and predict the values of J in similar oxido-bridges with other electronic configurations.

In Chapter 7, we further extended our synthetic approach to prepare manganese porphyrin species with targeted axial modification. These mono- and bis- axially substituted
complexes are found to catalyze olefin epoxidation effectively. The influences of axial substituents are discussed.
Synthesis, Structure, Magnetic and Electronic properties of Heterometallic Complexes Containing First-Row Transition Metals

by
Tao Huang

A dissertation submitted to the Graduate Faculty of North Carolina State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Chemistry

Raleigh, North Carolina

2016

APPROVED BY:

_________________________________________  _________________________________________
Dr. Walter Weare  Dr. Reza Ghiladi
Committee Chair

_________________________________________  _________________________________________
Dr. Elon Ison  Dr. David Shultz
DEDICATION

This work is dedicated to my grandmother Peiying Li, my parents Songmao Huang and Zhirong Xie, and my wife Yaqing Zhao. Thank you for your love, support and encouragement.
BIOGRAPHY

Tao Huang was born in Quanzhou, Fujian province, China in 1988 to a family of teachers. In July 2007, He graduated from Quanzhou No.5 Middle School with honor and then attended Wuhan University to pursue his undergraduate degree of chemistry. In 2009 he joined Prof. Bin Hu's group. His research focused on the determination of trace elements in drugs and medicines using inductively coupled plasma mass spectrometry (ICP-MS) techniques. He completed his Bachelors' degree in 2011 and then was admitted to Department of Chemistry in North Carolina State University for the graduate study. Since the fall of 2011, he joined Prof. Walter W. Weare's research group and has worked on the synthesis, structural characterization and magnetic properties of heterometallic complexes that consist of first-row-transition metals. He has presented his research at multiple meetings including the Solar Energy Research Center (SERC) Conference, South-Eastern Regional Meeting of the American Chemical Society (SERMACS), as well as several local meetings. During his time in the group, he has received the First Prize award in the poster-section at the 1st annual NC Photochem Symposium and a recognition of outstanding teaching assistant for organic chemistry lab.
ACKNOWLEDGMENTS

I want to gratefully and sincerely give my deepest thanks to my adviser, Prof. Walter W. Weare, for his guidance, attention and most importantly, his friendship during my graduate study. I would like to express the same gratitude to my committee members, Prof. Reza A. Ghiladi, Prof. Elon A. Ison and Prof. David A. Shultz for inspiring me to become an independent researcher and their academic support for achieving my goal. I would like to thank Dr. Roger D. Sommers, for his immense efforts in sharing the beautiful world of crystallography with me and the whole Shultz's group for the inspiration and mentorship of the "molecular magnetism". As may be seen in my thesis, the molecule's structure and magnetism are two major topics of discussion.

I also want to express my appreciation to my coworkers and labmates. Dr. Jürgen Bartelmess, Dr. Aaron Francis and Tyler Shogren, for providing excellent examples of work ethic, help and guidance for improving my skills and confidence as a chemist. My best partner Xinyuan Wu, for his persistent dedication and constant contribution to our projects. Le Li, Xiao Song and Prof. Tatyana Smirnova, for assistance in collecting EPR spectra. Dr. Daniel Stasiw for assistance in collecting magnetization data. Eric Goggins, Lifu Wang, Alec Frasois and Bryan Kim for the critical comments and suggestions for the thesis. The undergraduates Kyle Resco, Natalie Rice and Hao Xu, for their help and involvement of these projects.

Last, but not least, I must acknowledge my wife, Yaqing, for her unwavering love, continuing support and understanding. There are no words that can express my appreciation for your company and faith in me.
# TABLE OF CONTENTS

LIST OF TABLES ..................................................................................................................... x

LIST OF FIGURES .................................................................................................................. xi

CHAPTER 1 ............................................................................................................................... 1

1.1 Background ..................................................................................................................... 2

1.2 Experimental approach to measure magnetic coupling .................................................. 3

1.3 Rationalization of exchange coupling using superexchange theory ............................. 5

1.4 The model based on strict localized magnetic orbitals ................................................. 7

1.5 A quantitative expression for kinetic exchange interaction ........................................ 9

1.6 Conclusions .................................................................................................................. 12

1.7 References .................................................................................................................. 12

CHAPTER 2 ............................................................................................................................. 17

2.1 Abstract ......................................................................................................................... 18

2.2 Introduction .................................................................................................................. 18

2.3 Results and discussion ............................................................................................... 19

2.3.1 Synthesis and spectroscopic characterization ......................................................... 19

2.3.2 Crystal structures .................................................................................................. 25

2.3.3 Equilibrium studies ............................................................................................... 33

2.3.4 Electrochemical characterization ............................................................................ 36

2.3.5 Magnetic susceptibility ......................................................................................... 40
2.4 Conclusions......................................................................................................................... 42

2.5 Experimental section............................................................................................................. 43

2.5.1 General procedures. ......................................................................................................... 43

2.5.2 X-Ray crystallography ..................................................................................................... 46

2.5.3 Synthesis of chromium porphyrins .................................................................................. 46

2.5.4 Synthesis of (tmtaa)Ti═O→Cr(Por)Cl binuclear complexes ............................................ 48

2.5.5 Synthesis of [(tmtaa)Ti═O→Cr(Por)←O═Ti(tmtaa)]+ trinuclear complexes .... 49

2.6 Supporting information........................................................................................................ 53

2.7 Acknowledgements.............................................................................................................. 86

2.8 References.......................................................................................................................... 86

CHAPTER 3 ................................................................................................................................. 93

3.1 Abstract.............................................................................................................................. 94

3.2 Introduction........................................................................................................................ 94

3.3 Result and discussion.......................................................................................................... 96

3.4 Conclusion .......................................................................................................................... 108

3.5 Experimental section ........................................................................................................ 109

3.5.1 General procedures. ....................................................................................................... 109

3.5.2 X-Ray crystallography ................................................................................................... 111

3.5.3 Synthesis of (tmtaa)V═O→Cr(R)Cl binuclear complexes, ............................................. 111
3.5.4 Synthesis of [(omtaa)V═O→Cr(R)←O═V(omtaa)]⁺ trinuclear complexes,.... 112

3.5.5 Synthesis of [(tmtaa)Ti═O→Cr(R)←O═V(omtaa)]⁺ trinuclear complexes,.... 113

3.6 Supporting information........................................................................................................... 114

3.7 Acknowledgements.................................................................................................................... 130

3.8 References.................................................................................................................................... 130

CHAPTER 4 ...................................................................................................................................... 136

4.1 Abstract .................................................................................................................................... 137

4.2 Introduction ............................................................................................................................... 137

4.3 Result and discussion ................................................................................................................. 140

4.4 Conclusions ............................................................................................................................... 147

4.5 Supporting information .............................................................................................................. 148

4.6 Acknowledgements .................................................................................................................... 164

4.7 References .................................................................................................................................... 165

CHAPTER 5 ...................................................................................................................................... 169

5.1 Abstract .................................................................................................................................... 170

5.2 Introduction ............................................................................................................................... 170

5.3 Experimental ............................................................................................................................. 172

5.3.1 General procedures. ............................................................................................................... 172

5.3.2 X-Ray crystallography ........................................................................................................... 173

5.3.3 Preparation of L₁-L₄ .............................................................................................................. 173
5.3.4 General procedure of vanadium(IV) ion complexation.......................... 174
5.3.5 Complexation of manganese(II) ion.................................................... 175
5.4 Result and discussion.............................................................................. 177
5.4.1 Synthesis and characterization.............................................................. 177
5.4.2 Magnetic properties.............................................................................. 182
5.4.3 Cyclic voltammetry.............................................................................. 187
5.5 Conclusion.............................................................................................. 190
5.6 Supporting information........................................................................... 192
5.7 Acknowledgment.................................................................................... 213
5.8 References............................................................................................. 213
CHAPTER 6 .................................................................................................... 218
6.1 Abstract.................................................................................................. 219
6.2 Introduction............................................................................................ 219
6.3 Experimental.......................................................................................... 220
6.3.1 General procedures............................................................................ 223
6.3.2 X-Ray crystallography ....................................................................... 223
6.4 Result and discussion............................................................................ 224
6.4.1 Magnetic measurement....................................................................... 224
6.4.2 Determination of transfer integrals.................................................... 231
6.4.3 Estimation of J of different electronic configurations....................... 235
LIST OF TABLES

Table 1.1 Comparison of previous results of Goodenough-Kanomari rule and the refined results by Weihe and Güdel. 

Table 2.1 Comparison of binuclear complexic (1) and trinuclear complex (4) with the proposed binuclear complex of Goedken. The (tmtaa)Ti═O based electronic absorptions have been normalized to Soret peak to facilitate comparison.

Table 2.2 Selected bond lengths and angles for Cr(TMP)Cl•H₂O. 

Table 2.3 Crystal data and structure refinement details for Cr(TMP)Cl•H₂O. 

Table 2.4 Equilibrium constants for the reaction, (tmtaa)Ti═O + Cr(Por)Cl ⇌ (tmtaa)Ti═O → Cr(Por)Cl and (tmtaa)Ti═O + (tmtaa)Ti═O → Cr(Por)Cl ⇌ [(tmtaa)Ti═O→Cr(Por)═O

Table 2.5 Electrochemistry of (tmtaa)Ti=O, Cr(TMP)Cl•H₂O, 1-7 and 9-11. 

Table 2.6 Magnetic moment of 1-11. 

Table 3.1 Selected bond lengths and angles for 1-3. 

Table 3.2 Molar absorptivity of 1-3 in dichloromethane at 298 K and solid state ATR-FT-IR. 

Table 4.1 Selected structural parameters and J values for 1-3. 

Table 5.1 Redox potentials for L₄, 4 and 6. Signals are referenced to Fc/Fc⁺ at 0 V. 

Table 6.1 Expressions for the kinetic exchange interaction of J. 

Table 6.2 Expressions for the kinetic exchange interaction of J. 

Table 6.3 Selective structure parameters for 1-7. 

Table 6.4. Expressions for the kinetic exchange interaction of J in relative linear geometry. 

Table 6.5 Comparison between calculated and experimental results. 

Table 6.6 Schematic demonstration of proposed kinetic exchange pathways of 7. 

(B) The [1]₁→[1]₁ transfer interaction based on π overlap between Cu(dₓᵧ), O(pₓ) and V(dₓz). The final expression derived from these transfer integrals is given as Jₙₘ = +hₙ ὁ I + hₘ I’. 

Table 7.1 ATR-FTIR assignments of νₓ=O for 1-7.

Table 7.2 Summary of structural parameters for Mn(III)Por with mono- and bis axial substituents. 

Table 7.3 Epoxidation reaction of cyclohexene. Influence of catalyst, reaction time and axial ligand ratio. 

Table 7.4 Epoxidation reaction of trans-β-methylstyrene. Influence of different catalysts.

Table 7.5 Epoxidation reaction of cis-β-methylstyrene. Influence of different catalysts. 

Table 7.6 Epoxidation reaction of cis-β-methylstyrene. Formation of isomerization product.

x
LIST OF FIGURES

Figure 1.1 Schematic demonstration of $\left[\frac{1}{2}\right]_A \rightarrow \left[\frac{1}{2}\right]_B$ and $\left[\frac{1}{2}\right]_A \rightarrow [0]_B$ transfer integrals and their resulting stabilization in ground states. The $n_A$ and $n_B$ in this examples are 3 and 1, respectively. ................................................................. 11

Figure 2.1 A) Molar absorptivity of the precursor Cr(TPP)Cl, (mtaa)Ti=O and 1 and 4 in dichloromethane. B) Solid state ATR-FT-IR spectra of bimetallic complex 1 and trimetallic complex 4. $\nu_{\text{Ti}=\text{O}} = 901 \text{ cm}^{-1}$ for both 1 and 4. The intensity has been normalized to the peak at 1010 cm$^{-1}$. Full spectra can be found in the ESI. ................................................................. 25

Figure 2.2 X-ray crystal structure of Cr(TMP)Cl•H$_2$O. Thermal ellipsoids drawn at 50% probability. Hydrogen atoms (except those on H$_2$O) and solvent molecules are omitted for clarity. .......................................................................................................................... 27

Figure 2.3 X-ray crystal structure of bimetallic 2. Thermal ellipsoid plots are drawn at 50% probability. The hydrogen atoms, solvent molecules are omitted for clarity......................... 28

Figure 2.4 X-ray crystal structure of trimetallic complexes 10. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms, anion (SbF$_6^-$) and solvent molecules are omitted for clarity .................................................................................................................. 30

Figure 2.5 X-ray crystal structure of trimetallic complex 12. Thermal ellipsoids drawn at 50% probability. Hydrogen atoms (except those hydrogen bonding with chloride in the anion trap) and solvent molecules are omitted for clarity. ................................................................. 31

Figure 2.6 Packing view from the 001 plane of 12. Hydrogen atoms and solvent molecules are omitted for clarity. .................................................................................................................. 31

Figure 2.7 Cyclic voltammetry of complex 5 in degassed, dry dichloromethane with 0.1 M tetrabutylammonium hexafluorophosphate using glassy carbon working electrode, platinum counter electrode and silver wire quasi reference electrode. All signals were referenced to ferrocene/ferrocinium(Fe/Fe') at 0 V. The arrows a and b show the increasing current of process II and I in Figure 2.8, respectively................................................................. 39

Figure 2.8 X-band EPR spectra of Cr(TPP)Cl•H$_2$O, 1 and 8 at 298 K. *1 has a broader signal at around 3500 G which is due to minor paramagnetic impurities....................................................... 42

Figure 3.1 X-ray crystal structures of 1 and 3. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms, counter ions and solvent molecules are omitted for clarity............. 100

Figure 3.2 (A), Molar magnetic susceptibility (χpara) plotted as χpara•T vs. T for 1-3. Black lines represent the fit. (B) Variable field dependence of 1-3 at 2 K. (C), Exchange coupling J versus Cr–O bond distance for 1-3................................. 101

Figure 3.3 Experimental CW EPR spectra of 2 at 77 K (blue) and 298 K (green). Simulated spectra are also depicted for the E(5/2,1) ground (red) and E(3/2,0) first excited (magenta) magnetic states. E(S$_1$,S$_2$) is denoted as $S_1 = S_V + S_{V'} + S_{Cr}$, $S_2 = S_V + S_{V'}$............................................... 105

Figure 4.1 Comparison of the magneto-structural properties of 1-3. J$_{calc}$ is computed using previously reported empirical parameters with corrections from an angular overlap model.$^{30,32,47}$ .................................................................................................................. 139

Figure 4.2 Temperature-dependent magnetic susceptibility and variable-field magnetization (in-set) of 1-3. For comparison purposes, this data is not corrected for diamagnetic susceptibility. 1 has been previously reported.$^{37}$ .................................................................................................................. 142
Figure 4.3 (A) Schematic illustration of torsion effects on exchange coupling between two metallic sites. The $d_{t}-p_{\pi}$ overlap is minimal at a torsion degree of 45°. (B) The wing-up and wing-down configurations of (omtta)V=O. This results in disparate steric hindrances and is the origin of the twisted geometry in 2.

Figure 5.1 ATR-FTIR spectra of 1-4. The $v_{C=O}$ at ~ 1733 cm$^{-1}$ and $v_{C=O}$ at ~ 899 cm$^{-1}$ of 1 and 2 indicate non-coordinated carboxylic acid groups with V(IV) binding to the N$_2$O$_2$ site. The $v_{C=O}$ at ~ 1600 cm$^{-1}$ and $v_{C=O}$ at ~ 977 cm$^{-1}$ of 3 and 4 indicate the coordinated carboxylate groups with V(IV) binding to the O$_2$O$_2$ site.

Figure 5.2 X-ray crystal structures of mononuclear V(IV) complex 3 (V=O = 1.5953 Å) and heterometallic Mn(II)−V(IV) complex 6 (V=O = 1.5999 Å; Mn−V = 3.2415 Å; Mn−O−V = 102.3°). Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms and non-bonded solvent molecules are omitted for clarity.

Figure 5.3 Comparison of magnetic behavior of $d^{1}$-$d^{5}$ bimetallic Mn(II)-V(IV) under different conditions. (A). Temperature-dependent magnetic susceptibility for 6 (red) and a previously reported oxido bridge heterometallic Mn−O−V (blue). The fit is based on exchange spin Hamiltonian: $H = -2JS_v \cdot S_{Mn}$. (B). Variable field magnetization of 6 and Mn−O−V at 2 K. The structure (in-set) and magnetic study of Mn−O−V have been previously reported.

Figure 5.4 (A). The orthogonalized magnetic orbital description for Mn-O-V$^{38,41}$ based on kinetic exchange in C$_{s}$ symmetry. The d orbitals are labelled as $\epsilon$, $\zeta$, $\eta$ and $\theta$ for $x^2$-$y^2$, $yz$, $xy$, $xz$ and $z^2$, respectively. (B). The natural magnetic orbital description for 6 based on potential exchange in C$_{2v}$ symmetry.$^{27}$ The magnetic orbitals are labelled as $a_1$($xy$), $a_1^*(z^2)$, $a_2$($yz$), $b_1$($x^2$-$y^2$) and $b_2$($xz$) for the Mn(II) centered orbitals.

Figure 6.1 Temperature-dependent magnetic susceptibility ($\chi_T$ vs T) and variable-field magnetization at 2 K (in-set) for 3. The simulated Brillouin function is plotted with $S = 3$ and $g = 1.93$ for comparison.

Figure 6.2 Temperature-dependent magnetic susceptibility ($\chi_T$ vs T) and variable-field magnetization at 2 K (in-set) for 4. Diamagnetic susceptibility has been corrected according to Pascal constants.$^{78}$ The simulated Brillouin function is plotted with $S = 1/2$ and $g = 2.00$ for comparison.

Figure 6.3 Temperature-dependent magnetic susceptibility ($\chi_T$ vs T) and variable-field magnetization at 2 K (in-set) for 5. The simulated Brillouin function is plotted with $S = 2$ and $g = 2.00$ for comparison.

Figure 6.4 Temperature-dependent magnetic susceptibility ($\chi_T$ vs T) and variable-field magnetization at 2 K (in-set) for 6. The simulated Brillouin function is plotted with $S = 3/2$ and $g = 2.00$ for comparison.

Figure 6.5 Temperature-dependent magnetic susceptibility ($\chi_T$ vs T) and variable-field magnetization at 2 K (in-set) for 6. The simulated Brillouin function is plotted with $S = 1$ and $g = 1.96$ for comparison.

Figure 7.1 Crystal structures of mono- and bis-axially substituted species, A(1), B(5), C(6), D(7), E(10) and F(13). Thermal ellipsoids were drawn at the 50% probability level. Solvent molecules, hydrogen atoms and anions are omitted for clarity.
CHAPTER 1

General Introduction
1.1 Background

“More is different”, said by P.W. Anderson in 1972, means physical systems with larger scale and complexity may exhibit different behaviors in respect to their microscopic components. This idea is also valid in chemistry, since molecules can be modified to contain multiple functional group that enhance their chemical and physical properties. Nature is an expert at creating such heterofunctional systems. Relevant to the work in this thesis, enzymes are known to utilize a variety of heterometallic cores in order to perform different functions. Well-known examples include the Cu-Fe site in cytochrome oxidase, the Cu-Zn site superoxide dismutase and the Mn-Fe site in purple acid phosphatase. Synthetic heterometallic complexes also have a long and rich history of scientific investigation. New heterometallic molecules continue to be found that impact a wide varieties of research areas. As catalysts, heterometallic complexes are known to promote polymerization reactions and can improve selectivity in asymmetric reactions when compared to their individual components. As chromophores, heterometallic centers can undergo metal-to-metal charge transfer and act as photosensitizers in artificial photosynthetic systems. Heterometallic molecules can also be fundamental units in making functionalized materials, having been employed for applications in spin transport, molecular switches and single molecule magnets while showing promise for helping to achieve molecular-scale devices for electronics, magnetic data storage and quantum computing.

One of the central questions about the investigation of heterometallic systems is the understanding of the interactions between the metal centers in order to develop a method for understanding their structure-property relationships. This is of importance for improving the performance of heterobimetallic compounds in their varied applications. However, tuning the
properties of functionalized materials using molecular properties has never been a simple process. A potential alternate method for modeling the essential processes in complex systems is to study heterometallic molecules with similar structural fragments as those contained within such larger extended materials. For example, transition metal oxides are known to be promising magnetic materials. However, the quantum chemical basis for their functions at a molecular level were largely established utilizing model systems containing homometallic and heterometallic complexes. The properties elucidated include determining the sign and magnitude of exchange coupling within polynuclear centers, theoretical analysis on the origins of such interactions and the establishment of magneto-structural relationships that have been used to tune the properties of the overall material.

In this document we describe our studies into the metal-metal interactions across one of the simplest of bridging units, the oxido-bridge. We will discuss our synthesis of heterometallic complexes containing first-row transition metals and their chemical and structural characterization (Chapter 2-5). Finally, we explore their magnetic properties and structure-property relationships (Chapter 3-6). An introduction into the fundamental theories that can describe such magnetic interactions are further explained in the rest of Chapter 1.

1.2 Experimental approach to measure magnetic coupling.

When two metal centers (A and B) have unpaired electrons (n_A and n_B), their possible local spin number and local spin states are S_A = n_A/2, 2^{S_A+1}Γ_A and S_B = n_B/2, 2^{S_B+1}Γ_B, respectively. The magnetic interactions between A and B may then be decomposed into several terms as shown in equation (1),

\[ \hat{H}_{AB} = -2J\hat{S}_A\hat{S}_B + \hat{S}_A D_A\hat{S}_A + \hat{S}_B D_B\hat{S}_B + \hat{S}_A D_{AB}\hat{S}_B \] (1)
The first component of this equation represents the isotropic interaction between A and B, where J is a scalar. This expression shows the energy difference between the two coupled spin states, which are \(|S_A - S_B|\) and \(S_A + S_A\). When J is positive, the two spin centers are ferromagnetically coupled, with a high spin \(S_A + S_A\) state being the lowest lying state. On the other hand, when J is negative the low spin state \(|S_A - S_B|\) is the lowest in energy. The second and third terms are the local anisotropic interactions, which split the \(2S+1\) \(\Gamma\) pair states when under zero field if \(S > 1/2\). The fourth term represents the anisotropic interaction, which would result in a splitting of the coupled state under zero field. Local and coupled spin states can be split under zero field due to spin orbital coupling and local distortions.\(^{50,51}\) However, such local anisotropies and anisotropic interactions can also lead to a splitting of the \(2S+1\) \(\Gamma\) states. For simplicity, this contribution can be, and often is, ignored with the dominant interaction being expressed as the isotropic interaction in equation (2). A specific example which further considers these anisotropic interactions is discussed in Chapter 6.

\[
\hat{H}_{AB} = -2J\hat{S}_A\hat{S}_B \tag{2}
\]

In order to compute the energy difference between the \(2|S_A-S_B|\) \(\Gamma_{AB}\) and \(2(S_A+S_B)+1\) \(\Gamma_{AB}\) states, equation (2) can be modified using the following equation (3),

\[
\hat{S}_{tot}^2 = (\hat{S}_A + \hat{S}_B)^2 = \hat{S}_A^2 + \hat{S}_B^2 + 2\hat{S}_A\hat{S}_B, \quad \hat{S}_A\hat{S}_B = \frac{(\hat{S}_{tot}^2 - \hat{S}_A^2 - \hat{S}_B^2)}{2} \tag{3}
\]

The eigenvalues for \(\hat{H}\) can be expressed as in equation (4),

\[
E_n = -J[S_{tot}(S_{tot} + 1) - S_A(S_A + 1) - S_B(S_B + 1)] \tag{4}
\]

These equations can then be combined using the Heisenberg Dirac van Vleck\(^{40}\) approach, as shown in equation (5),
\[ \chi = \frac{N g^2 \beta^2}{3k_B T} \sum_S S(S+1)(2S+1)e^{-\frac{E_S}{k_B T}} \sum_S (2S+1)e^{-\frac{E_S}{k_B T}} \]  

(5)

This allows one to experimentally determine the exchange coupling constant J by measuring temperature-dependent magnetic susceptibility. However, it has to be noted that this Hamiltonian is a simple concept which does not provide direct information on the mechanism of the computed interactions. Additional work is necessary to describe the physical meanings behind the computed values obtained by this method.

1.3 Rationalization of exchange coupling using superexchange theory

In order to rationalize a physical meaning for the exchange coupling value J, several different models have been developed. This is important since a physical description is required to theoretically predict how to modify this important term in real molecules. A widely accepted model is using a superexchange interaction to describe magnetic coupling. This has been particularly useful in explaining the insulator properties of metallic oxide materials. A detailed discussion of superexchange interactions between paramagnetic metal ions, which are connected through diamagnetic ions, was initially explained by Kramers in 1934.\(^\text{52}\) Kramers proposed that the fundamental concept for superexchange interactions is the mixing of excited state character into the ground states in small amount. This approach was further refined by Anderson in 1950,\(^\text{53}\) which formulated superexchange into a series of interactions. The relationship of the ligand environment and orbital orientation have been further examined by Goodenough\(^\text{54}\) and formulated by Kanomari,\(^\text{55}\) which resulted in a more rigorous mathematical
treatment. Their approach is widely used as the Goodenough-Kanomari rules, which qualitatively explain magnetic interactions within polymetallic complexes and materials.

According to Anderson’s theory,\textsuperscript{40,53-57} when a bridged bimetallic system (AXB) is controlling the magnetic interactions, the interaction between two ions is expressed between their magnetic orbitals \(a\) (for A site) and \(b\) (for B site). In the simplest case, these magnetic orbitals can be constructed using the molecular orbitals on A \((\phi_1)\) and B \((\phi_2)\) through equation (6).

\[
a = \frac{\phi_1 + \phi_2}{\sqrt{2}}, \quad b = \frac{\phi_1 - \phi_2}{\sqrt{2}}
\]  

(6)

The magnetic orbitals of \(a\) and \(b\) are obviously orthogonal to each other. However, these magnetic orbitals can be delocalized, with the tail of the \(a\) wavefunction able to be delocalized to create overlap with the \(b\) wavefunction. This can be qualitatively understood as being similar in shape to the virtual antibonding portion of the A-X bond. In this case, the energy gap \(J\) is given by equation (7),

\[
J = J_F + J_{AF} = 2k - \frac{4\beta^2}{U}
\]  

(7)

where \(k\) is defined as the Coulombic repulsion integral between the two electronic centers shown in equation (8). \(r_{12}\) represents the distance between the two electronic centers. \(k\) is then a two electron integral and is always a positive quantity, indicating that electronic repulsion between two spin centers should force ferromagnetically coupled states due to a potential exchange interaction using Hund’s rule. The second term of equation (7) represents the
negative contribution of $J$, and is known as the kinetic exchange interaction which originates from the mixing of charge transfer excited states into the ground state configurations. The magnitude of this term is proportional to the electronic coupling between $a$ and $b$, shown in equation (9). This kinetic exchange interaction is inversely proportional to $U$, which is the energy required for an exchange interaction to happen.

Beyond this electron-electron interaction between two unpaired electrons, additional factors also need to be considered.\(^{58}\) In particular, magnetic orbitals originating on one metal can interact with empty orbitals on a second metal center. Such interactions contribute to additional ferromagnetic interactions.\(^{58}\) Such superexchange theories as proposed by Anderson, Goodenough and Kanomari have been applied successfully to many experimental examples.\(^{34,59-61}\) However, due to the necessary inclusion of delocalized magnetic orbitals, such models are can be challenging to visualize, resulting in difficulty when utilizing these concepts to qualitatively predict the magnitude of magnetic interaction in complex systems.\(^{44}\)

1.4 The model based on strict localized magnetic orbitals

In order to solve the perceived defects in superexchange theory, Kahn\(^{40,43-45,56,57}\) developed an alternative model based on magnetic orbitals which are strictly localized on each metal center. In this model, Kahn assumed that the magnetic exchange interaction is similar to a very weak bonding interaction.\(^{62}\) Since there are several models that can explain bonding interactions, strongly delocalized electronic interactions have been explained using the molecular orbital description of Hund and Mulliken.\(^{63}\) On the other hand, when interactions are weak, electrons are assumed to be localized which can be described utilizing the valence bond model as proposed by Heiter and London.\(^{34}\) In a similar manner, Kahn’s model may be
viewed as a borderline weak chemical bond where valence bond theory concepts can explain the magnetic interactions between paramagnetic centers.

In this model, magnetic orbitals are localized in the form shown, with individual metal orbitals being, in general, non-orthogonal to one other. This leads to the concept of natural magnetic orbitals. Using natural magnetic orbitals, an additional one-electron integral is necessary, namely the overlap integral $S$, equation (10):

$$ S = \langle a(1) | b(1) \rangle $$  \hspace{1cm} (10)

In this case, the magnetic orbital $a$ in AXB is defined as the singly occupied molecular orbitals for the AX fragment in its local ground state, with $b$ being similarly defined with respect to the XB fragment.\(^{40}\) The energy gap is therefore given as equation (11)

$$ J = J_F + J_{AF} = 2k + 4\beta S - 2S^2 (2\alpha + j) - \frac{4[\beta + l - (a + j + k)S]^2}{U} $$  \hspace{1cm} (11)

The electron integrals are represented in either the one electron integral of equations 12-13 and as a two electron integral using equations 14-16

One-electron integrals:

$$ \alpha = \langle a(1) | h(1) \rangle a(1) \rangle $$  \hspace{1cm} (12)

$$ \beta = \langle a(1) | h(1) \rangle b(1) \rangle $$  \hspace{1cm} (13)

Two-electron integrals:

$$ j = \langle a(1) b(2) | 1/r_{12} | a(1) b(2) \rangle $$  \hspace{1cm} (14)

$$ k = \langle a(1) b(2) | 1/r_{12} | a(2) b(1) \rangle $$  \hspace{1cm} (15)

$$ l = \langle a(1) b(2) | 1/r_{12} | b(1) b(2) \rangle $$  \hspace{1cm} (16)

In Kahn’s model an antiferromagnetic contribution arises primarily from the second term of equation 11 ($4\beta S$), since $\beta$ and $S$ have different signs. In many cases, equation 11 can be
simplified since the third term \( (2S^2(2\alpha+J)) \) become negligible when when S is small. The final term is the interaction that results from mixing charge transfer excited states with ground states, and results in an antiferromagnetic contribution. However, Kahn\(^{40} \) assumed this mixing can also be ignored. This ultimately results the following simplified expression (equation 17).

\[
J = J_F + J_{AF} = 2k + 4\beta S
\]  

(17)

The main difference between this expression and Anderson’s theory is that the antiferromagnetic interaction using the natural magnetic orbital approach is assumed to be a weak bonding interaction between magnetic orbitals due to the overlap, with the ferromagnetic interaction arising entirely from the potential interaction \( 2k \). This therefore predicts that when the magnetic orbitals \( a \) and \( b \) are strictly orthogonal, \( \beta \) and \( S \) are zero by definition and the resulting value for \( J \) is a ferromagnetic potential interaction that has a magnitude of \( 2k \).

According to Kahn’s experiments and ab initio computations, such potential exchange interactions can be as large as \(+60 \text{ cm}^{-1}\).\(^{42,45} \) However, it has to be noted that in Kahn’s model excited state mixing is entirely ignored. This suggests that when a system involves delocalized magnetic orbitals with obvious charge transfer mixing (such as in systems with an observable metal-to-metal charge transfer band), this model may not be quantitatively or qualitatively valid.

1.5 A quantitative expression for kinetic exchange interaction

Kahn’s model is especially useful in understanding the ferromagnetic contribution of the potential interaction in molecules which can be adequately described using localized magnetic orbitals. However, when this potential interaction is weak, i.e. in the oxido-bridged complexes described in this thesis, the ferromagnetic interactions that originate from the kinetic exchange model may still be important due to the presence of significant mixing of the charge transfer
excited states with the high spin ground states. Due to a lack of accurate expressions from previous theoretic treatments, Weihe and Güdel mathematically formulated this model.\textsuperscript{46} The important transfer integrals are defined in Table 1, which I have compared with the summarized formulas of Goodenough.\textsuperscript{46} As described in Table 1, four fundamental charge transfer processes originate from the kinetic exchange model of Anderson and can be mathematically expressed and related to different contributions of the charge transfer integrals (Figure 1).\textsuperscript{49} These are: i) the half to half transfer ($[\frac{1}{2}]_A \rightarrow [\frac{1}{2}]_B$), which is the process where the electron is taken from a half-filled orbital of one metal and moved to a half-filled orbital on the second metal (this interaction will always be antiferromagnetic), (ii) the half to zero transfer ($[\frac{1}{2}]_A \rightarrow [0]_B$), which represents the process when an unpaired electron is taken from a half-filled orbital on one metal and moved into an empty orbital on a second metal (this is found to be a ferromagnetic interaction), (iii) the one to half transfer ($[1]_A \rightarrow [\frac{1}{2}]_B$), which is when an electron is taken from a full orbital on one metal and moved into a half-filled orbital on the second metal (this has been identified as ferromagnetic) and (iv) the one to half transfer $[1]_A \rightarrow [0]_B$, which is when an electron is taken from a full orbital on one metal and moved into an empty orbital on a second metal (this process can result in either ferromagnetic or antiferromagnetic interactions, depending on $n_A$ and $n_B$). The applications of this method to our work have previously discussed in more detail\textsuperscript{49,64} and are included in Chapter 3-6.
Table 1.1 Comparison of previous results of Goodenough-Kanomari rule and the refined results by Weihe and Güdel.\textsuperscript{46}

<table>
<thead>
<tr>
<th>Interaction Type\textsuperscript{a}</th>
<th>Early GK’s rule</th>
<th>Expression by Güdel\textsuperscript{46}</th>
<th>Label</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\frac{1}{2}]_A \rightarrow [\frac{1}{2}]_B$</td>
<td>$- \frac{1}{n_A n_B} h_{ij}^2 U$</td>
<td>$- \frac{1}{n_A n_B} h_{ij}^2 U$</td>
<td>(20)</td>
</tr>
<tr>
<td>$[\frac{1}{2}]_A \rightarrow [0]_B$</td>
<td>$+ \frac{1}{n_A n_B} h_{ij}^2 I$</td>
<td>$+ \frac{1}{n_A U} h_{ij}^2 I$</td>
<td>(21)</td>
</tr>
<tr>
<td>$[1]_A \rightarrow [\frac{1}{2}]_B$</td>
<td>$+ \frac{1}{n_A n_B} h_{ij}^2 I$</td>
<td>$+ \frac{1}{n_B U} h_{ij}^2 I$</td>
<td>(22)</td>
</tr>
<tr>
<td>$[1]_A \rightarrow [0]_B$</td>
<td>ferromagnetic</td>
<td>$- \frac{(n_A - n_B)}{(n_A + 1)(n_B + 1)} \frac{h_{ij}^2 I}{U}$</td>
<td>(23)</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The original expressions are based on $\hat{H}_{ab} = +J_{ab} \hat{S}_a \hat{S}_b$, while we use $\hat{H}_{ab} = -2J_{ab} \hat{S}_a \hat{S}_b$. The “-2” fold difference is applied in the final expressions.

Figure 1.1 Schematic demonstration of $[\frac{1}{2}]_A \rightarrow [\frac{1}{2}]_B$ and $[\frac{1}{2}]_A \rightarrow [0]_B$ transfer integrals and their resulting stabilization in ground states. The $n_A$ and $n_B$ in this examples are 3 and 1, respectively.
1.6 Conclusions

As a summary, understanding the metal-metal interactions can be achieved through the combination of experimental measurement and theoretical modelling. Anderson's model has provided the framework for connecting the spin-spin interaction with charge transfer excited states, which is more suitable for systems that may potentially undergo metal-metal charge transfer. On the other hand, Kahn's model treats such magnetic interaction as weak bonding interactions, and is more applicable for systems with closed intermetallic distance. Moreover, such model is based on localized magnetic orbitals and would simplify the virtualization of such spin-spin interactions. Through the discussion of this thesis, both models will be concerned and explained on a case-by-case basis.

1.7 References


(52) Kramers, H. A. Physica 1934, 1, 182.


CHAPTER 2

Mono-oxido-bridged heterobimetallic and heterotrimetallic compounds containing titanium(IV) and chromium(III)

This work was published in Eur. J. Inorg. Chem.


Huang, T performed all general characterization work and worked with Sommer, R. D. to conduct X-ray diffraction experiment. The synthesis was perform by Huang, T and Wu, X.

Department of Chemistry, North Carolina State University;

Raleigh, NC, 27695-8204
2.1 Abstract

A series of oxido-bridged hetero bi- and trimetallic complexes (tmtaa)Ti═O→Cr(Por)Cl and [(tmtaa)Ti═O→Cr(Por)←O═Ti(tmtaa)]+ (tmtaa = 7,16-dihydro-6,8,15,17-tetramethyldibenzo[b,i][1,4,8,11]tetraazacyclotetradecine; Por = 5,10,15,20-tetraarylporphyrin) have been synthesized. To our knowledge, these complexes are the first structurally characterized examples that contain a Ti═O→Cr or Ti═O→Cr←O═Ti structural motif. Crystal structures of representative heterobimetallic compounds, including the Ti═O→Cr binuclear complex 2 and two separate trimers, [Ti═O→Cr←O═Ti]SbF₆ 10 and [Ti═O→Cr←O═Ti]Cl 12, are reported. The bimetallic and trimetallic molecules have similar structural parameters, including Ti−O, Cr−O and Ti−O−Cr bond lengths within a linear Ti═O→Cr geometry. Magnetic studies show that a high spin CrIII (S = 3/2) center is present in both the binuclear and trinuclear molecules. The redox potentials for CrIV/II/III (ΔE = 320 mV) and Por/Por+ (ΔE = 260 mV) can be tuned by altering the identity of the porphyrin ligand. By determining the thermodynamics and kinetics for the formation of these complexes using titration and electrochemistry, it was found that the bimetallic and trimetallic species undergo isomerization in solution, allowing for easy substitution of the apical chlorido ligand.

2.2 Introduction

Heterometallic oxido bridged complexes remain an understudied area of synthetic transition metal chemistry.¹ Several recent studies addressing the assembly of oxido-bridged heterobimetallic molecules on the surface of heterogeneous supports have revealed that such systems can be used as chromophores for photon-driven chemistry, including water oxidation or CO₂ reduction.²⁻¹¹ Absorption by metal-to-metal charge transfer (MMCT) transitions is believed to be responsible for the observed photochemical reactivity.¹²⁻¹⁵ However, molecular
systems containing unsupported mono-oxido bridges of first-row transition metals are rare. Structural reports for heterobimetallic mono-oxido bridged compounds with d-electrons include Ti−O−V,\textsuperscript{16} Ti═O→Fe,\textsuperscript{17} V═O→Fe,\textsuperscript{18} V═O→Mn,\textsuperscript{19} Cr−O−Fe,\textsuperscript{20,21} Fe−O−Co,\textsuperscript{22} Fe−O−Cu\textsuperscript{23} with a singular example of Ti−O−Cr\textsuperscript{24} that was recently reported by our group. Only two structures of heterotrimetallic oxido-bridged compounds are known to date, each containing a Fe−O−Ru−O−Fe linkage.\textsuperscript{25,26}

Synthesis and characterization of soluble, molecular compounds containing a Ti−O−Cr core are of interest to obtain a further understanding of chromophores based on MMCT from chromium(III) to titanium(IV).\textsuperscript{4-6} Goedken reported a synthetic method for mono-oxido-bridged heterobimetallic complexes where a titanium terminal oxido complex, (tmtaa)Ti═O (tmtaa = 7,16-dihydro-6,8,15,17-tetramethyldibenzo[b,i][1,4,8,11]tetraazacyclotetradecine), was used as a Lewis base to form coordination complexes with Lewis acidic metal centers such as Cr\textsuperscript{III}salen and Cr\textsuperscript{III}porphyrin.\textsuperscript{17} However, the structural, spectroscopic and electrochemical properties of these complexes have not yet been reported. Here, we report the synthesis and characterization of a series of heterobimetallic and heterotrimetallic Ti═O→Cr compounds, finding that the reactivity and physical properties of this system are more complex than initially described.

This is the first definitive report of heterobimetallic and heterotrimetallic complexes utilizing (tmtaa)Ti═O. By rigorously characterizing the complex behavior of this system, we have been able to rationally control molecular properties such as electrochemical potential and absorptivity.\textsuperscript{27-31}

2.3 Results and discussion

2.3.1 Synthesis and spectroscopic characterization
The reaction between (tmtaa)Ti═O and Cr(Por)Cl can proceed to form either the bimetallic or trimetallic species depending on the stoichiometry. As shown in Scheme 2.1, the heterobimetallic complex, Ti═O→Cr, is obtained as the primary product when a titanium to chromium ratio of 1:1 is used. The heterotrimetallic compound is obtained as the primary product when the titanium to chromium ratio is greater than 2:1. Addition of (tmtaa)Ti═O to the Ti═O→Cr binuclear complexes also forms the heterotrimetallic complex [Ti═O→Cr←O═Ti][Cl]. As discussed later, chloride is in equilibrium with the second equivalent of (tmtaa)Ti═O. Therefore, more stable complexes are obtained after either anion exchange of the chloride to yield the [Ti═O→Cr←O═Ti][SbF$_6$], or coordination of the chloride using anion traps such as calix[4]pyrroles.

**Scheme 2.1.** Synthesis of Ti═O→Cr binuclear complexes 1-3 and trimeric [Ti═O→Cr←O═Ti]* complexes 4-11

i) 1:1 ratio of (tmtaa)Ti═O and Cr(Por)Cl;  ii) 1:2 ratio of (tmtaa)Ti═O and Cr(Por)Cl, iii) 1:2:1.1 ratio of (tmtaa)Ti═O, Cr(Por)Cl and NaSbF$_6$. 

<table>
<thead>
<tr>
<th>Heterobimetallic</th>
<th>X = Cl; X = SbF$_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>R = phenyl, (TPP)</td>
<td>4 8</td>
</tr>
<tr>
<td>R = 4-methoxyphenyl, (TMP)</td>
<td>5 9</td>
</tr>
<tr>
<td>R = 4-fluorophenyl, (TFP)</td>
<td>6 10</td>
</tr>
<tr>
<td>R = 4-(trifluoromethyl)phenyl, (TFMP)</td>
<td>7 11</td>
</tr>
</tbody>
</table>

Heterotrimetallic

1: R = phenyl
2: R = 4-methoxyphenyl
3: R = naphthyl, (TNAP)
As shown in Scheme 2.1, the heterobimetallic Ti=O→Cr binuclear complexes 1-3 can be obtained when a titanium to chromium ratio of 1:1 is employed. The yield varies from 50% to 73% depending on the porphyrin used. When synthesizing complexes 1 and 2, the Ti=O→Cr binuclear complex is the major product. However, a small amount of the [Ti=O→Cr←O=Ti][Cl] trinuclear complexes and homocoupled (tmtaa)Ti=O ([Ti−O−Ti]Cl2)32,33 is also observed. These side products are much less soluble than the binuclear complexes, and are thus easily separated by filtration from the reaction mixture. Complex 3 precipitates readily from solution in both high yield and purity. We were unable to observe the formation of the corresponding heterotrimer of complex 3, even after addition of excess (tmtaa)Ti=O.

By adjusting the stoichiometry of CrIII-Porphyrin and (tmtaa)Ti=O to 1:2, complexes 4-7 can be obtained as dark green precipitates in a one pot reaction. The isolated yield after further recrystallization varies from 46% to 65% depending on the porphyrin. Compounds 8-11, which contain a hexafluoroantimonate anion instead of chloride, are obtained by adding 1.1 equivalents of NaSbF6 to the synthesis, with isolated yields ranging from 37% ~ 53%. Complex 12 (Scheme 2.2) was collected as X-ray quality orange plate crystal on flask wall when excess H4TFMP was added into a refluxing solution of complex 7.
Scheme 2.2. Synthesis of [Ti═O→Cr←O═Ti][Cl] trinuclear complex complex 12. The anion trap H₄TFMP is further described in ESI Figure 2.S1.

Although complex 1 was reported by Goedken from a reaction of 1:1 Ti═O and Cr(TPP)Cl, we have found that the reaction is more complicated than previously described. In particular, Goedken indicated that the Ti═O→Cr “heterobimetallic” complex has an indicative Soret peak at 454 nm in addition to two (tmtaa)Ti═O based peaks at 342 nm and 388 nm. Although we observe similar peaks in the Ti═O→Cr binuclear complexes and [Ti═O→Cr←O═Ti]⁺ trinuclear complexes, the molar absorptivity of the (tmtaa)Ti═O based peaks (342 and 388 nm) reported by Goedken are similar to the [Ti═O→Cr←O═Ti]⁺ trinuclear complex (Table 2.1). We conclude that the molecule reported by Goedken is actually the heterotrimetallic species 4 (presumably separated due to its low solubility), and not the claimed heterobimetallic species 1. The EAS spectra comparing the precursors (Cr(TPP)Cl, (tmtaa)Ti═O), bimetallic complex 1 and trimetallic complex 4 is depicted in Figure 2.1. The Soret band is red shifted by ~ 8 nm due to deformation of the porphyrin. The (tmtaa)Ti═O based absorption features at 328 nm (LMCT) and 377 nm (π-π*) are significantly red shifted to 345 nm and 390 nm respectively upon coordination to the chromium center. In the trimetallic species these bands have a molar absorptivity twice of that for bimetallic species, consistent with our assignment.
Table 2.1 Comparison of binuclear complexic (1) and trinuclear complex (4) with the proposed binuclear complex of Goedken. The (tmtaa)Ti═O based electronic absorptions have been normalized to Soret peak to facilitate comparison.

<table>
<thead>
<tr>
<th></th>
<th>(tmtaa)Ti═O based,</th>
<th>Soret,</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binuclear 1</td>
<td>344 (0.50)\textsuperscript{[a]}, 396 (0.53)</td>
<td>452 (1.00)</td>
</tr>
<tr>
<td>Trinuclear 4</td>
<td>344 (0.94), 390 (1.04)</td>
<td>456 (1.00)</td>
</tr>
<tr>
<td>“Binuclear”\textsuperscript{[b]}</td>
<td>342 (1.26), 388 (1.20)</td>
<td>454 (1.00)</td>
</tr>
</tbody>
</table>

\textsuperscript{[a]} Normalized intensity. \textsuperscript{[b]} Trinuclear complex 4, but was assigned as binuclear complex in previous work.\textsuperscript{17}

Solid state ATR-FTIR spectrum of (tmtaa)Ti═O shows a single sharp band around 920 cm\textsuperscript{-1},\textsuperscript{1,35} which is assigned to $\nu_{\text{Ti═O}}$.\textsuperscript{33,17} This peak is known to red shift by 10 - 50 cm\textsuperscript{-1} when (tmtaa)Ti═O is coordinated to different Lewis acids.\textsuperscript{17} We have found that in compounds 1-12 this peak is located between 916 cm\textsuperscript{-1} to 894 cm\textsuperscript{-1}, which further confirms the formation of a $\mu$-oxido bridge in these complexes –Figure 2.1 and ESI. The lower energy of $\nu_{\text{Ti═O}}$ indicates that when the oxygen interacts with chromium it weakens the Ti═O bond, presumably through $\sigma$ donating and $\pi$ donating/accepting interactions from the oxygen to the chromium. Thus, a larger red shift of $\nu_{\text{Ti═O}}$ implies a stronger Ti═O→Cr interaction. Among those compounds, complex 3 has a particularly weak Ti═O→Cr bond, which is rationalized by the steric effect of the bulky naphthyl substituents on the porphyrin. Although the other complexes have relatively similar $\nu_{\text{Ti═O}}$, we are able to observe electronic effects from the porphyrin substituents. For example, electron donating substituents weaken the dative interaction between the chromium and oxygen centers, resulting in $\nu_{\text{Ti═O}} = 909$ cm\textsuperscript{-1} for methoxy (9). Electron withdrawing substituents such as fluoro (10) display a $\nu_{\text{Ti═O}}$ at 894 cm\textsuperscript{-1} and are consistent with stronger dative interactions to a more electron-poor Cr\textsuperscript{III} center. These observations are consistent with (tmtaa)Ti═O acting as both a $\sigma$- and a $\pi$-donor, and suggests
that in this case such binding modes dominate over the known π-acceptor behavior.\textsuperscript{17} For complexes 8-11, an additional peak around 656 cm\textsuperscript{-1} is observed, which is assigned to ν\textsubscript{Sb-F}.\textsuperscript{36}

Despite the small differences in energy of ν\textsubscript{Ti═O} between bimetallic and trimetallic species, we find that the relative intensity of this peak is doubled in the trimetallic species when compared to that of the bimetallic complexes. This behavior is similar to what is observed in the EAS for the intensity of the (tmtaa)Ti═O centered absorptions (λ\textsubscript{max} = 345 nm and 390 nm). This observation also distinguishes between the bimetallic and trimetallic complexes. (Figure 2.1)
Figure 2.1 A) Molar absorptivity of the precursor Cr(TPP)Cl, (tmtaa)Ti═O and 1 and 4 in dichloromethane. B) Solid state ATR-FT-IR spectra of bimetallic complex 1 and trimetallic complex 4. νTi=O = 901 cm⁻¹ for both 1 and 4. The intensity has been normalized to the peak at 1010 cm⁻¹. Full spectra can be found in the ESI.

2.3.2 Crystal structures

We were able to grow crystals suitable for XRD study of 2, a direct analog of 1 and 3. The growth of X-ray quality single crystals using TMP was used in early structural studies of metalloporphyrins.³⁷ The chloride salts of trimetallic complexes (4-7) afforded poor quality structures in all cases, with badly disordered chloride and solvent positions that were unresolvable. We conclude from our equilibrium constant studies (see next section for detail) that their instability precludes the formation of suitable crystals in most cases. Introducing SbF₆ increases the stability of trimetallic complexes 8-11 and facilitates the growth of single crystals.
Table 2.2 Selected bond lengths and angles for Cr(TMP)Cl•H₂O, 2,10,12

<table>
<thead>
<tr>
<th>Summary</th>
<th>Cr(TMP)Cl•H₂O 2</th>
<th>10</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr-Cl distance (Å)</td>
<td>2.3225(10)</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Ti-O distance (Å)</td>
<td>n/a</td>
<td>1.6829(16)</td>
<td>1.683(3)</td>
</tr>
<tr>
<td>Cr-N avg. distance (Å)</td>
<td>2.034(3)</td>
<td>2.0324(19)</td>
<td>2.027(3)</td>
</tr>
<tr>
<td>Ti-N avg. distance (Å)</td>
<td>n/a</td>
<td>2.037(2)</td>
<td>2.033(3)</td>
</tr>
<tr>
<td>Cr-O distance (Å)</td>
<td>2.066(3)</td>
<td>1.9413(15)</td>
<td>1.938(3)</td>
</tr>
<tr>
<td>Ti-O-Cr angle (°)</td>
<td>n/a</td>
<td>176.99(11)</td>
<td>178.18(18)</td>
</tr>
<tr>
<td>O-Ti-N avg. angle (°)</td>
<td>n/a</td>
<td>109.35(8)</td>
<td>109.23(13)</td>
</tr>
<tr>
<td>O-Cr-N avg. angle (°)</td>
<td>88.29(11)</td>
<td>88.96(7)</td>
<td>90.00(12)</td>
</tr>
</tbody>
</table>

However, the large void spaces and the unresolved solvent positions still posed problems for structure refinement. A reasonable structure of 10 was obtained by use of SQUEEZE to remove unresolved electron density. Connectivity–only structures for 8 and 9 were also found that corroborate the trimetallic structure. Other large anions including tetrakis[3,5-bis(trifluoromethyl)phenyl]borate were used, but satisfactory X-ray quality crystal was still not obtained. The problem of solvent and anion disorder was ultimately addressed by adding the H₄TFMP calix[4]pyrrole as an anion trap (Scheme 2.2, Scheme 2.S1 and see Figure 2.5, crystal structure of 12 for details).
Figure 2.2 X-ray crystal structure of Cr(TMP)Cl•H$_2$O. Thermal ellipsoids drawn at 50% probability. Hydrogen atoms (except those on H$_2$O) and solvent molecules are omitted for clarity.

We found that H$_4$TFMP occupies previously empty space in the unit cell as well as trapping the chloride anion.$^{40-44}$ For comparison with the structure of bimetallic complex 2, Cr(TMP)Cl•H$_2$O was prepared according to the literature.$^{45}$ Crystals suitable for X-ray diffraction were obtained in slow vapor diffusion from di $n$-butyl ether to dichloromethane. Cr(TMP)Cl•H$_2$O is known, but its structure (Figure 2.2) has not been previously reported.
The crystal structure of 2 is depicted in Figure 2.3, confirming the bimetallic configuration shown in Scheme 2.1. (tmtaa)Ti═O coordinates in the axial position of Cr(TMP)Cl forming a μ-oxido bridge. An interesting feature of all of the heterometallic structures is observed with the tmtaa ligand, which undergoes a complete saddle inversion when compared to the structure of (tmtaa)Ti═O.\textsuperscript{17} To our knowledge, such a “phenyl-down” ligand geometry has only been observed once before for tmtaa complexes, in the structurally similar bimetallic compound ((TPP)Cr−O−Fe(tmtaa)) reported by West.\textsuperscript{21} Complex 2 has a Ti═O bond length of 1.6829(16) Å (Table 2.2) and Cr−O bond length of 1.9413(15) Å. The Ti═O bond length is slightly longer than that of (tmtaa)Ti═O (1.653(3) Å),\textsuperscript{17} but is shorter than in the previously reported
bimetallic molecules Ti═O→Fe (1.701(6) Å)\textsuperscript{17} and Ti─O─Cr (1.779(2) Å).\textsuperscript{24} This short bond length indicates that the Ti═O still retains multiple bond character. The Cr─O bond is significantly longer than previously described bimetallic molecules Fe─O─Cr (1.776(11) Å)\textsuperscript{21} and Ti─O─Cr (1.850(2) Å)\textsuperscript{24} and is consistent with the proposed dative interaction. However, the bond length is shorter than in the similar dative bond (Cr─OH\textsubscript{2}) in Cr(TMP)Cl•H\textsubscript{2}O (2.066(3) Å) and any other axial O-donor coordinated Cr\textsuperscript{III} porphyrins, suggesting that (tmtaa)Ti═O is more tightly bound than other O-donor Lewis bases.\textsuperscript{46,47} The Ti─O─Cr bond angle is nearly linear with an angle of 176.99(11)°, which is considerably larger than in the bent Ti─O─Cr linkage of covalent systems (166.88(14)°).\textsuperscript{24} The Cr─Cl bond length of 2.3577(6) is found 0.03 Å longer than that of Cr(TMP)Cl•H\textsubscript{2}O, which is 2.3225(10) Å. The increase of the Cr─Cl bond length is consistent with a structural-trans-influence, which is described in detail elsewhere.\textsuperscript{47,48}

The structure of trimetallic complexes 10 and 12 are depicted in Figures 4 and 5, and have similar Ti─O─Cr geometries as 2. Two (tmtaa)Ti═O groups are coordinated to the chromium center in a staggered geometry. The bond length and angle of Ti─O─Cr in 10 and 12 are almost identical to those observed for 2 and are summarized in Table 2.2. The (tmtaa)Ti═O unit has a shorter Cr─O distance (1.9413(15) Å) than other similar datively bond species, such as Ph\textsubscript{3}P═O\textsuperscript{47} (2.033(4) Å) and H\textsubscript{2}O\textsuperscript{46} (2.057(2) Å). This suggests that (tmtaa)Ti═O is a better ligand under these conditions than other simple oxygen donor Lewis bases.
In complex 12, the chloride was immobilized in a porphyrinogen calix[4]pyrrole (H₄TFMP) anion trap. The structural parameters of the anion trap consistent with previous studies. From the packing map of complex 12 (Figure 2.6), we find the H₄TFMP has comparable size as the trimetallic complex, and they align linearly to form an organized architecture in the solid state. Although porphyrinogens are known to be air sensitive, complex 12 is stable in both solution and the solid state when exposed to air. We believe that the electron withdrawing groups may play a role in this stabilization.
Figure 2.5 X-ray crystal structure of trimetallic complex 12. Thermal ellipsoids drawn at 50% probability. Hydrogen atoms (except those hydrogen bonding with chloride in the anion trap) and solvent molecules are omitted for clarity.

Figure 2.6 Packing view from the 001 plane of 12. Hydrogen atoms and solvent molecules are omitted for clarity.
### Table 2.3 Crystal data and structure refinement details for Cr(TMP)Cl·H₂O, 2.10.12

<table>
<thead>
<tr>
<th>Identification code</th>
<th>Cr(TMP)Cl·H₂O</th>
<th>2</th>
<th>10</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCDC</td>
<td>1001312</td>
<td>999173</td>
<td>1000580</td>
<td>999100</td>
</tr>
<tr>
<td>Formula</td>
<td>C₅₁H₄₁N₁₇O₄Cl</td>
<td>C₇₂H₆₂Cl₃CrN₆O₂</td>
<td>C₆₉H₆₈N₁₂O₂F₁₀Ti₂C</td>
<td>C₁₅₀H₁₁₇ClCrF₂₄N₂₁O₂</td>
</tr>
<tr>
<td>Mw</td>
<td>961.43</td>
<td>1396.44</td>
<td>1785.09</td>
<td>2880.86</td>
</tr>
<tr>
<td>T /K</td>
<td>110(2)</td>
<td>110.1</td>
<td>110.1</td>
<td>110(2)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
<td>orthorhombic</td>
<td>monoclinic</td>
<td>tetragonal</td>
</tr>
<tr>
<td>Space group</td>
<td>Pn</td>
<td>P₂₁₂₁</td>
<td>P₂₁/n</td>
<td>P₄/n</td>
</tr>
<tr>
<td>a /Å</td>
<td>14.8022(6)</td>
<td>16.0177(7)</td>
<td>16.0036(8)</td>
<td>23.1810(7)</td>
</tr>
<tr>
<td>b /Å</td>
<td>9.1685(4)</td>
<td>19.5409(8)</td>
<td>24.1922(10)</td>
<td>23.1810(7)</td>
</tr>
<tr>
<td>c /Å</td>
<td>18.1960(7)</td>
<td>20.1114(9)</td>
<td>23.4013(12)</td>
<td>12.5405(4)</td>
</tr>
<tr>
<td>α /°</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β /°</td>
<td>99.490(2)</td>
<td>92.667(2)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>γ /°</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Volume/Å³</td>
<td>2435.66(17)</td>
<td>6294.9(5)</td>
<td>9050.3(7)</td>
<td>6738.7(5)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>4</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>ρcalc,mg/mm³</td>
<td>1.311</td>
<td>1.473</td>
<td>1.31</td>
<td>1.42</td>
</tr>
<tr>
<td>m/mm⁻¹</td>
<td>0.346</td>
<td>0.573</td>
<td>0.654</td>
<td>0.311</td>
</tr>
<tr>
<td>F(000)</td>
<td>1002</td>
<td>2884</td>
<td>3620</td>
<td>2954</td>
</tr>
<tr>
<td>Crystal size/mm³</td>
<td>0.28 x 0.2 x</td>
<td>0.876 x 0.285 x</td>
<td>0.345 x 0.299 x</td>
<td>0.26 x 0.2 x 0.12</td>
</tr>
<tr>
<td>Radiation</td>
<td>MoKα (λ = 0.71073)</td>
<td>MoKα (λ = 0.71073)</td>
<td>MoKα (λ = 0.71073)</td>
<td>MoKα (λ = 0.71073)</td>
</tr>
<tr>
<td>2Θ range for data collection</td>
<td>3.294 to 56.564°</td>
<td>3.25 to 62.844°</td>
<td>3.018 to 54.094°</td>
<td>4.08 to 59.16°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-19 ≤ h ≤ 19, -23 ≤ h ≤ 23, -28 ≤ k ≤ 17, -29 ≤ l ≤ 24</td>
<td>-20 ≤ h ≤ 20, -30 ≤ k ≤ 30, -29 ≤ l ≤ 29</td>
<td>-28 ≤ h ≤ 31, -32 ≤ k ≤ 32, -17 ≤ l ≤ 17</td>
<td></td>
</tr>
<tr>
<td>Reflections collected</td>
<td>38323</td>
<td>140213</td>
<td>135401</td>
<td>72806</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>11094 [Rint = 0.0522, Rsigma = 0.0511]</td>
<td>20785 [Rint = 0.0338, Rsigma = 0.0259]</td>
<td>19818 [Rint = 0.0426, Rsigma = 0.0307]</td>
<td>9429 [R(int) = 0.0293]</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>11094/2/621</td>
<td>20785/0/883</td>
<td>19818/0/1053</td>
<td>9429/1/487</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.046</td>
<td>1.043</td>
<td>1.054</td>
<td>1.047</td>
</tr>
<tr>
<td>Final R indexes</td>
<td>R₁ = 0.0479, wR₂ = 0.1231</td>
<td>R₁ = 0.0347, wR₂ = 0.0892</td>
<td>R₁ = 0.0676, wR₂ = 0.1528</td>
<td>R₁ = 0.0437, wR₂ = 0.1147</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>R₁ = 0.0529, wR₂ = 0.1274</td>
<td>R₁ = 0.0416, wR₂ = 0.0936</td>
<td>R₁ = 0.0894, wR₂ = 0.1669</td>
<td>R₁ = 0.0617, wR₂ = 0.1268</td>
</tr>
<tr>
<td>Largest diff. peak/hole / e Å⁻³</td>
<td>0.50/-0.36</td>
<td>0.78/-0.54</td>
<td>1.98/-3.50</td>
<td>0.56/-0.58</td>
</tr>
</tbody>
</table>
2.3.3 Equilibrium studies

In order to unambiguously determine the stoichiometry and binding constants that enables the synthesis of these compounds, we utilized a titration method previously reported by Hoffman and coworkers. They found that the Cr−Cl binding constant (log K) in Cr(TPP)Cl(S) (where S = σ bases such as H$_2$O or imidazole) was quite large, having a lower limit of 6.71 (See ESI for a full description of this method). The stoichiometry of both Cr(TPP)Cl and Cr(TNAP)Cl with (tmtaa)Ti═O is determined to be 1:1 for the first addition of (tmtaa)Ti═O. The first equilibrium constants (logK$_1$) were found to be 3.72 and 3.32, respectively (Table 2.4). In contrast to the work by Hoffman, who were unable to displace the chlorido ligand with any N-, O- or S-donor, we found that addition of a second equivalent of (tmtaa)Ti═O to 1 cleanly forms the heterotrimetallic 4. The equilibrium constant for this second step (logK$_2$ = 2.67) is significantly smaller than the first step (logK$_1$ = 3.72). This result is consistent with the ability to isolate bimetallic compounds 1-3, and implies that an equilibrium is present between the trimetallic and bimetallic complexes in solution.

<table>
<thead>
<tr>
<th>Acceptor</th>
<th>Product</th>
<th>N</th>
<th>log K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(TPP)Cl</td>
<td>1</td>
<td>1.04</td>
<td>3.72</td>
</tr>
<tr>
<td>Cr(TNAP)Cl</td>
<td>3</td>
<td>1.03</td>
<td>3.32</td>
</tr>
<tr>
<td>1</td>
<td>4</td>
<td>1.04</td>
<td>2.67</td>
</tr>
<tr>
<td>3</td>
<td>No product formed</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>
At this point, it is necessary to comment on the previously observed strong binding constant for Cr−Cl (log $K > 6.71$) and ask why the second equivalent of $(tmtaa)\text{Ti}=\text{O}$ is able to displace the chlorido ligand under these conditions. In our opinion, the chlorido replacement in our system is explainable in two ways. First, the initial $(tmtaa)\text{Ti}=\text{O}$ labilizes the chlorido ligand via a donating (presumably both $\sigma$ and $\pi$) mechanism. Second, the $\text{trans}$ complexes are stabilized via a push-pull mechanism (presumably through $\pi$ interactions) that is not possible with the previously studied N-, O- and S- donor ligands.

It has been proposed that $(tmtaa)\text{Ti}=\text{O}$ acts similarly to CO to form $\sigma$ bonds and $\pi$ back bonds with transition metals. Since the chlorido ligand is a $\sigma$ donating ligand, and a weak $\pi$ donor, the $\sigma$ donating interaction from the first $(tmtaa)\text{Ti}=\text{O}$ could be the main factor that contributes to destabilizing the bonding between the chromium and chlorido. This labilization of $\text{trans}$ ligand via $\sigma$ donating path in porphyrin has been described in detail in a previous review. If a $\pi$ back bonding interaction between $(tmtaa)\text{Ti}=\text{O}$ and chromium porphyrin was present it would result in a situation where it is less favorable to have the second $(tmtaa)\text{Ti}=\text{O}$ coordinate vs. even the weakly $\pi$ donating chlorido. This effect has been observed in studies of Fe, Co, Ru and Os porphyrins, where strong $\pi$-acceptor ligands are destabilizing when located $\text{trans}$ to one another. In contrast, the decrease of $\nu_{\text{Ti}=\text{O}}$ in 3 and 4, compared to 1 and 2 respectively, suggest that the bonding interactions between $(tmtaa)\text{Ti}=\text{O}$ and chromium are instead strengthened in these trinuclear complexes. The equilibrium constants also quantitatively indicate that the second $(tmtaa)\text{Ti}=\text{O}$ is significantly more stable than chlorido after the first $(tmtaa)\text{Ti}=\text{O}$ is added to the chromium center. Therefore, an additional interaction must be present to further stabilize the trinuclear system. Thus we propose that $(tmtaa)\text{Ti}=\text{O}$ is also a $\pi$-donating ligand, which serves to weaken the Cr−Cl $\pi$-donor bond and enable the
displacement of the chlorido ligand. Here, this interaction allows for the addition of a second equivalent of (tmtaa)Ti═O, but other ligands could also be introduced. The mutual function of π-donor and π-acceptor of the two trans (tmtaa)Ti═O ligands also enables a push-pull interaction as previously observed in other systems. This effect also can further stabilize the trinuclear complexes.

The equilibrium constant of the reaction between (tmtaa)Ti═O and the sterically bulky Cr(TNAP)Cl (log $K_1$=3.32) was found to be slightly smaller than that of Cr(TPP)Cl (log $K_1$=3.72). Unlike the other heterobimetallic compounds, addition of excess (tmtaa)Ti═O to 3 did not generate the corresponding trimetallic species. We propose that the presence of the first (tmtaa)Ti═O blocks the binding of a second ligand due to the directionality of the naphthyl substituents on the porphyrin. Even addition of excess NaSbF$_6$, which facilitates the dissociation of chloride, was unable to induce formation of the trimetallic compound. Further discussion of this effect can be found in the ESI.

In summary, although the binding constant for the first ligand to Cr(TPP)Cl is related to the magnitude of that ligand’s pK$_a$, binding of a second ligand is not only simply linearly related to its pK$_a$, but also influenced by π donating/accepting ability of axial ligands. Thus it is not surprising that (tmtaa)Ti═O is capable to replace chlorido while other stronger bases are unable to do so. The combination of σ donating effect and mutual π accepting/donating effect of (tmtaa)Ti═O allows various types of trans ligands such as chlorido and (tmtaa)Ti═O to be stably isolated. From the equilibrium constants, the binding of the second (tmtaa)Ti═O to the (tmtaa)Ti═O→Cr fragment is energetically ($\Delta G = -15.2 \text{ kJ/mol}$) more favorable than binding of chlorido. We propose that this effect can be used to synthesize unsymmetric six
coordinated chromium porphyrin complexes using (tmtaa)\(\text{Ti} \equiv \text{O}\rightarrow \text{Cr} \equiv \text{Cl}\) as a universal precursor.

### 2.3.4 Electrochemical characterization

Cyclic voltammetry data for trimetallic complexes 1-7 and 9-11 are summarized in Table 2.5 and depicted in Figure 2.S4-7. (tmtaa)\(\text{Ti} \equiv \text{O}\) was observed to be irreversibly oxidized at 0.53 V (vs. Fc/Fc\(^+\), as for all other reported potentials) and be reduced at -2.36 V. Since (tmtaa)\(\text{Ti} \equiv \text{O}\) has \(d^0\) configuration in the metal, the oxidation at 0.53 V must be ligand centered. No reduction is observed for tmtaa, thus the -2.36 V wave is assigned as the \(\text{Ti}^{\text{IV/III}}\) couple. The electrochemical processes of the chromium porphyrin monomers was assigned as previously reported.\(^{65-67}\) The redox process of \(\text{Cr(TMP)Cl\cdotH}_2\text{O}\) at potentials of 0.91V, 0.44 V, -1.25 V, -1.73 V, -2.40 V are assigned as the eletrogeneration of the porphyrin \(\pi\) cation radical, Cr(IV), Cr(II), porphyrin \(\pi\) anion radical and porphyrin dianion, respectively. Interpretation of the cyclic voltammetry data of 1-7, 9-11 are based on perturbations of the conclusions from the monomers. Recent studies\(^{67}\) of the chromium porphyrin oxidation states are also considered, where it is suggested that Cr(II)TPP is more accurately expressed as Cr(III)TPP\(^-\) in almost all cases.

When comparing \(\text{Cr(TMP)Cl\cdotH}_2\text{O}\) with binuclear complex 2, the formation of the \(\text{Ti} \equiv \text{O}\rightarrow \text{Cr}\) bonding cathodically shifts the \(\pi\) cation formation from 0.79 V to 0.69 V, but the magnitude of change in the Cr\(^{\text{IV/III}}\) couple (0.36 V to 0.33 V) and \(\pi\) anion formation (-1.73 V to -1.72 V) are relatively small. In contrast, the cathodic shift of \(\pi\) cation formation (0.79 V to 0.72 V) is relative smaller than that of Cr\(^{\text{IV/III}}\) couple (0.36 to 0.22 V) and \(\pi\) anion formation (-1.73 V to -1.86 V). These abnormal variations of potentials are the net influence of porphyrin deformation and electron donating effect from axial ligands. The first \(\pi\) cation formation from
0.79 V to 0.69 V is mainly from removing one electron from porphyrin $a_{2u}$ orbital. Ruffling of the porphyrin caused by the first (tmtaa)Ti═O addition will destabilize the $a_{2u}$ orbital of the porphyrin. In the trinuclear 9, this potential shifts less anodically (to 0.72 V) even though the porphyrin is more ruffled relative to the binuclear 2. This could be explained by including an interaction between the $d_{xy}$ of Cr and the $a_{2u}$ in of the porphyrin. These orbitals are of the same symmetry in the D$_{2d}$ point group, and are likely to have similar energies when the ruffling degree is large. The resulting interaction between $d_{xy}$ and $a_{2u}$ would stabilize $a_{2u}$, causing the observed anodic shift.

Table 2.5 Electrochemistry of (tmtaa)Ti=O, Cr(TMP)Cl•H$_2$O, 1-7 and 9-11.[a][b]

<table>
<thead>
<tr>
<th>Compound</th>
<th>Eox3</th>
<th>Eox2</th>
<th>Eox1</th>
<th>Ered1</th>
<th>Ered2</th>
</tr>
</thead>
<tbody>
<tr>
<td>(tmtaa)Ti=O</td>
<td>-</td>
<td>-</td>
<td>0.53</td>
<td>-2.36</td>
<td>-</td>
</tr>
<tr>
<td>Cr(TPP)Cl[c]</td>
<td>0.91</td>
<td>0.44</td>
<td>-1.67</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr(TMP)Cl•H$_2$O[c]</td>
<td>-</td>
<td>0.79</td>
<td>0.36</td>
<td>-1.73</td>
<td>-2.40</td>
</tr>
<tr>
<td>1</td>
<td>-</td>
<td>0.81</td>
<td>0.43</td>
<td>-1.70</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>0.69</td>
<td>0.33</td>
<td>-1.72</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>0.74</td>
<td>0.48</td>
<td>-1.70</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>-</td>
<td>0.85</td>
<td>0.38</td>
<td>-1.78</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>-</td>
<td>0.74</td>
<td>0.25</td>
<td>-1.83</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>-</td>
<td>0.88</td>
<td>0.41</td>
<td>-1.74</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>-</td>
<td>1.01</td>
<td>0.59</td>
<td>-1.60</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>1.10</td>
<td>0.72</td>
<td>0.22</td>
<td>-1.86</td>
<td>-2.37</td>
</tr>
<tr>
<td>10</td>
<td>1.07</td>
<td>0.86</td>
<td>0.39</td>
<td>-1.76</td>
<td>-2.32</td>
</tr>
<tr>
<td>11</td>
<td>1.23</td>
<td>0.98</td>
<td>0.54</td>
<td>-1.60</td>
<td>-2.16</td>
</tr>
</tbody>
</table>

[a] Cyclic voltammetry were perform in degassed, dry CH$_2$Cl$_2$ with 0.1 M tetrabutylammonium hexafluorophosphate using glassy carbon working electrode, platinum counter electrode and silver wire quasi reference electrode. All signals were referenced to
ferrocene/ferrocenium(Fc/Fc⁺) at 0 V. [b] Compound 8 decomposes in CH₂Cl₂ when tetrabutylammonium hexafluorophosphate is present
[c] The Cr³⁺/²⁺ is irreversible for porphyrin monomer in CH₂Cl₂, Cr³⁺/²⁺ of Cr(TPP)Cl and Cr(TMP)Cl is observed at -1.47 V and -1.45 V respectively.

The cathodic shifts of Cr⁴⁺/³⁺ and the π anion are not surprising given by the influence of the σ and π donating⁵⁵,⁶⁶ (tmtaa)Ti═O and the resulting increased π back bonding from chromium dₓ to porphyrin π*,⁵⁵ respectively. Noteworthy, the change from binuclear to trinuclear species is more significant than that from porphyrin monomer to binuclear species. In addition, the change in the tmtaa ligand-centered oxidation is large (0.53 V to 1.10 V in 9) when (tmtaa)Ti═O is coordinated to chromium porphyrin. This large anodic shift is caused by the large structural change of the ligand geometry in (tmtaa)Ti═O, upon formation of the complex (a complete saddle inversion).

When comparing the relatively electron donating porphyrin 9 to the relatively electron withdrawing porphyrin in 11, all of the potentials were anodically shifted by 0.26~0.32 V, except for the tmtaa centered oxidation peak, which did not undergo a significant change (0.03 V). This relative small influence on tmtaa oxidation is expected, as only the porphyrin energetics are being synthetically modified.³⁴ The Ti⁴⁺/³⁺ couple is beyond the solvent window and was not observed. The potentials observed at -2.16 V to -2.37 V in compound 9-11 are due to further reduction of the chromium porphyrin, forming either Cr²⁺-Por⁻ or the porphyrin dianion. The change in the potentials across the series is consistent with this assignment.

The one electron reduction of Cr³⁺ porphyrin is directly related to its axial substituents and can be used to identify the ligated ligands.⁷⁰ In order to determine the stability of these complexes, cyclic voltammetry of 5 was performed at varying scan-rates. For the quasi-reversible Por/Por⁺ couple,⁷⁰ a single peak was observed at a relatively slow scan rate (50
mV/s), which became two distinctive reversible peaks at higher scan rates (200 mV/s). (Figure 2.7) This result can be explained using the square scheme mechanism proposed by Kadish,\textsuperscript{66} As shown in Figure 2.S8, a trimetallic 5 can generate reduced bimetallic 2 in two discrete pathways. In the presence of chloride, ligand exchange to form a bimetallic intermediate can occur. The Por/Por\textsuperscript{+} couple redox potential of the bimetallic species is similar to that of the trimetallic species, and two close peaks are observed at high scan rates. We propose that this is a direct observation of the ligand exchanged intermediate – a more detailed discussion of this effect is found in the ESI.

**Figure 2.7** Cyclic voltammetry of complex 5 in degassed, dry dichloromethane with 0.1 M tetrabutylammonium hexafluorophosphate using glassy carbon working electrode, platinum counter electrode and silver wire quasi reference electrode. All signals were referenced to ferrocene/ferrocenium(Fc/Fc\textsuperscript{+}) at 0 V. The arrows a and b show the increasing current of process II and I in Figure 2.S8, respectively.
2.3.5 Magnetic susceptibility

Several experimental techniques have been used to determine the magnetic susceptibility of heterobimetallic and heterotrimetallic complexes. These include Evan’s method\textsuperscript{71} (1-11), electron paramagnetic resonance spectroscopy (EPR)\textsuperscript{72} (1, 8) and using a superconducting quantum interference device (SQUID)\textsuperscript{73} (8).

The effective magnetic moments (\( \mu_{\text{eff}} \)) were measured via Evan’s method at room temperature and are summarized in Table 2.6. Diamagnetic correction parameters were calculated from Pascal’s constant\textsuperscript{74} with additional correction being applied as reported for metalloporphyrins.\textsuperscript{75} The heterobimetallic complexes show an overall \( \mu_{\text{eff}} \) close to 3.8 \( \mu_{\text{B}} \), which is in agreement with high spin (\( S = 3/2 \)) Cr\textsuperscript{III}. The heterotrimetallic complexes show an overall \( \mu_{\text{eff}} \) in the range between 3.03~3.87 \( \mu_{\text{B}} \). The relative small effective magnetic moment compared to the binuclear species either suggests that the trimetallic compound is a mixed ground state electronic configuration (\( S = 1/2 \) and \( S = 3/2 \)) (presumably due to porphyrin deformation) or there is a systematic underestimation of the diamagnetic correction in the triminuclear species. Such an effect is known in large supramolecular assemblies.\textsuperscript{76} To confirm the ground state electronic configuration of Cr\textsuperscript{III}, the magnetic properties of 8 were further studied using SQUID magnetometry. As shown in Figure 2.S13, magnetization saturation was performed at 2 K from 0-70000 Oe with the maximized value obtained being 2.86 \( \mu_{\text{B}} \), consistent with the presence of 3 unpaired electrons in 8. Temperature dependent magnetic susceptibility was measured from 2 K to 300 K (See Figure 2.S14). There is no observable contribution from \( S = 1/2 \), ruling out the presence of a mixed \( S = 1/2 \) and \( S = 3/2 \) state. Therefore we conclude that the Cr\textsuperscript{III} center is high spin d\textsuperscript{3} at all temperatures for these molecules.
This assignment is further confirmed by powder X-band EPR. The X-band EPR spectra of Cr\textsuperscript{III} porphyrin has been studied and discussed in detail in previous publications.\textsuperscript{54,77} The magnitude of zero field splitting (ZFS) in \textit{S}= 3/2 tetragonal Cr\textsuperscript{III} is known to result in qualitatively distinct EPR signals. EPR spectra of representative monomer (Cr(TPP)Cl•H\textsubscript{2}O), binuclear complex \textbf{1} and trimer \textbf{8} are shown in Figure 2.8. Each has a similar appearance, which indicates similar electronic configurations for the Cr\textsuperscript{III} ion in each case. This result is consistent with previous results where Cr(TPP)Cl was ligated with axial O-donor ligands.\textsuperscript{54} Visual comparison of this data with known ZFS parameter values for Cr\textsuperscript{III} complexes\textsuperscript{54,77,78} indicates that the ZFS parameter |D| is approximately 0.23 cm\textsuperscript{-1} with an isotropic g = 1.98.\textsuperscript{77}

\textbf{Table 2.6 Magnetic moment of 1-11}

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\mu\text{eff} \ (\mu\text{B}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binuclear complex</td>
<td></td>
</tr>
<tr>
<td>\textbf{1} (TPP) \textsuperscript{[a]}</td>
<td>3.87</td>
</tr>
<tr>
<td>\textbf{2} (TMP) \textsuperscript{[a]}</td>
<td>3.70</td>
</tr>
<tr>
<td>\textbf{3} (TNAP) \textsuperscript{[a]}</td>
<td>3.61</td>
</tr>
<tr>
<td>\textbf{4} (TPP) \textsuperscript{[a]}</td>
<td>3.39</td>
</tr>
<tr>
<td>\textbf{5} (TMP) \textsuperscript{[a]}</td>
<td>3.70</td>
</tr>
<tr>
<td>\textbf{6} (TFP) \textsuperscript{[b]}</td>
<td>3.20</td>
</tr>
<tr>
<td>Tinuclear complex</td>
<td></td>
</tr>
<tr>
<td>\textbf{7} (TFMP) \textsuperscript{[b]}</td>
<td>3.82</td>
</tr>
<tr>
<td>\textbf{8} (TPP) \textsuperscript{[a]}</td>
<td>3.30</td>
</tr>
<tr>
<td>\textbf{9} (TMP) \textsuperscript{[a]}</td>
<td>3.03</td>
</tr>
<tr>
<td>\textbf{10} (TFP) \textsuperscript{[b]}</td>
<td>3.37</td>
</tr>
<tr>
<td>\textbf{11} (TFMP) \textsuperscript{[b]}</td>
<td>3.11</td>
</tr>
</tbody>
</table>

\textsuperscript{[a]} In CDCl\textsubscript{3} \textsuperscript{[b]} In CD\textsubscript{2}Cl\textsubscript{2}
Figure 2.8 X-band EPR spectra of Cr(TPP)Cl·H$_2$O, 1 and 8 at 298 K. *1 has a broader signal at around 3500 G which is due to minor paramagnetic impurities.

2.4 Conclusions

Twelve Cr–O–Ti heterobimetallic and heterotrimeatallic complexes are reported, which to our knowledge are the first structurally characterized heterotrimeatallic examples containing this molecular configuration. Although the heterobimetallic 1 was previously reported, we find that the chemistry of this system is more complex than initially realized and the trimetallic 4 was most likely the compound isolated under the published conditions. Structurally, these molecules have linear, unsupported $\mu$-oxido linkages with bond lengths consistent with dative interactions between chromium and the Ti=O ligand. We were also able to block formation of trinuclear species through the presence of sterically demanding meso-naphtyl groups. Both the bimetallic and trimetallic complexes are shown to be high spin Cr$^{III}$ ($S = 3/2$). The obtained
ZFS constant ($|D| \sim 0.23 \text{ cm}^{-1}$, $g = 1.98$) is in good agreement with previous literature for a Cr$^{III}$ porphyrin with axial O-donor ligands.

It has been reported the Cr(TPP)Cl has an unusually strong Cr−Cl binding constant,\textsuperscript{54} but we have found that (tmtaa)Ti═O efficiently replaces the chlorido ligand. The equilibrium constants at 298 K for the first equivalent of (tmtaa)Ti═O with Cr$^{III}$porphyrin is shown to be log $K_1 = 3.72$ and the second equivalent is log $K_2 = 2.67$. The analysis of cyclic voltammetry data of 1-7, 9-11, reveals the redox potential is affected by addition of (tmtaa)Ti═O and porphyrin deformation. The redox properties of Cr$^{III/II}$ ($\Delta E = 320 \text{ mV}$) and Por/Por$^-$ ($\Delta E = 260 \text{ mV}$) can be tuned by altering the identity of the porphyrin ligand, while the electrochemistry of the (tmtaa)Ti═O fragments remain relatively unchanged. Variable scan rate cyclic voltammetry study of 5 indicates that a fast equilibrium is present that generates both trimetallic and bimetallic complexes. These results demonstrate that we can independently vary the redox potentials of heterobimetallic complexes, which will assist in the future design of tunable MMCT chromophores.

Synthetically, the ability to selectively make both heterobimetallic and heterotrimetallic complexes suggests that (tmtaa)Ti═O can be used to control the lability of trans ligands in Cr$^{III}$porphyrins. We anticipate that this approach will prove to be general for other $\pi$-donors and metalloporphyrins.

2.5 Experimental section

2.5.1 General procedures.

All reactions were performed under an atmosphere of nitrogen in an Innovative Technology glovebox or using Schlenk techniques. All used chemicals were purchased from VWR International, Sigma Aldrich, Alfa Aesar, and TCI America and were used without further
purification except as noted. Deuterated NMR solvents: benzene-\(d_6\) (C\(_6\)D\(_6\)) and deuterated chloroform (CDCl\(_3\)) were purchased from Cambridge Isotope Laboratories, Inc. All solvents were stored over 4Å molecular sieves prior to use. Dichloromethane, pentane, and tetrahydrofuran, were sparged with N\(_2\) and dried over an alumina column using the method of Grubbs.\(^79\) Toluene, diethylether and C\(_6\)D\(_6\) were dried over purple sodium benzophenone ketyl, then vacuum transferred and freeze-pump-thawed before storing in Teflon-sealed Schlenk bombs. Acetonitrile was dried over CaH\(_2\) and distilled prior to use. CDCl\(_3\) was deoxygenated with three cycles of freeze-pump-thaw and stored over 4Å molecular sieves prior to use. Water free dimethylformamide was purchased from VWR, and was briefly exposed to vacuum prior to use. (tmtaa)\(\text{Ti} \equiv \text{O}\)\(^{17}\) was prepared according to literature procedures. The 5,10,15,20-tetraarylporphyrins employed in this study are represented by the following abbreviations: TPP, tetraphenylporphyrin; TMP, tetrakis(4-methoxyphenyl)porphyrin; TFP, tetrakis(4-fluorophenyl)porphyrin, TFMP, tetrakis((4-trifluoromethyl)phenyl)porphyrin; TNAP, tetrathenaphthyl porphyrin. The free base porphyrinogen 5,10,15,20-tetrakis((4-trifluoromethyl)phenyl) porphyrinogen is represented as H\(_4\)TFMP.

\(^1\)H, \(^{13}\)C and \(^{19}\)F-NMR were recorded on a Varian Mercury 400MHz spectrometer. Chemical shifts are reported with reference to solvent resonances \(^1\)H NMR (ref C\(_6\)D\(_6\): 7.16 ppm; CDCl\(_3\):7.26 ppm.) \(^{13}\)C NMR (ref CDCl\(_3\) = 77 ppm) and \(^{19}\)F NMR (ref 4-(trifluoromethyl)benzaldehyde = -62.7 ppm).\(^80\) Absorption spectra were recorded on an Olis RSM-1000 spectrometer using Teflon-sealed quartz cuvettes. Attenuated total reflectance (ATR) FT-IR spectra were recorded on a Bruker Vertex 80V infrared spectrometer equipped with a Platinum™ diamond ATR attachment. See ESI for representative \(^1\)H NMR, \(^{13}\)C NMR and ATR-FTIR spectra. Electrochemical measurements were acquired on a BioLogic SP-200
potentiostat/galvanostat using a glassy carbon as working electrode, Ag/Ag\(^+\) reference electrode, and Pt wire counter electrode. Cyclic voltammetry was performed in a N\(_2\) atmosphere glovebox in dichloromethane solution and referenced to Fc/Fc\(^+\) = 0 V, with 0.1 M tetra-n-butylammonium hexafluorophosphate (TBAHFP) electrolyte. The scan rate was 200 mV/s unless otherwise noted. High resolution exact mass spectrometry measurements-EIS (HRMS-ESI) were carried out on a high resolution mass spectrometer (MS) (Thermo Fisher Scientific, Exactive Plus mass spectrometer) using Heated Electrospray Ionization (HESI). Samples were dissolved in dry dichloromethane and acetonitrile and analyzed via flow injection into the mass spectrometer at a flow rate of 200 µL/min. Evan’s method\(^71\) was used to measure the magnetic moments. Diamagnetic correction was accomplished using Pascal’s constant,\(^74\) with extra correction for porphyrins (\(\chi_{\text{dia}} = -7\times10^{-3}\) emu/mol) as previously described.\(^81\) Magnetic susceptibilities were measured on a Quantum Design MPMS-XL7 SQUID Magnetometer. A saturation plot was measured at 2 K with an applied field varied from 0~70000 oe. A Curie plot was obtained from varying the temperature with an applied field of 7000 oe. Crystalline samples (ca. 10-30 mg) were loaded into gelcap/straw sample holders and mounted to the sample rod with Kapton tape for temperature dependence measurements. Electron paramagnetic resonance spectra were taken on a Bruker ELEXSYS E500 spectrometer operating at approximately 9.86 GHz (X-band) at room temperature with a modulation amplitude of 10 G and a modulation frequency of 100 kHz. The experimental time constant was set at 81.92 ms with a 117.19 ms conversion time and a 120 s sweep time. A typical collection of 1024 data points is performed under 2 mW incident microwave power in a range from 0 to 8000 G. Recrystallized polycrystalline solid samples (1 ~ 2 mg) were loaded in Wilmad\(^\circledR\) quartz (CFQ) EPR tubes (O.D. 4 mm, L 100 mm) and sealed under N\(_2\). The
approximate zero-field-splitting parameter $|D|$ is determined by comparison with the schemes as previously reported.$^{54,77,78}$

2.5.2 X-Ray crystallography

Crystals were mounted on MiTeGen mounts and cooled to 110 K. X-ray intensity data were measured on a Bruker-Nonius X8 Kappa APEX II system equipped with a graphite monochromator and a MoKα fine-focus sealed tube ($\lambda = 0.71073$ Å). Unit cell dimensions were determined from symmetry constrained fits of the reflections. Frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the multi-scan method (SADABS). Structures were solved using direct methods (Bruker XS) and refined using the Bruker SHELX 2013 software package using full-matrix least-squares refinement on F. All non-hydrogen atoms were identified in the original solution, or located from the difference map from refinement results. Hydrogen atoms were placed at idealized positions and allowed to ride on the nearest non-H atom. Figures of the molecular structures were created using Olex2 Crystallographic information files for all structures are available in the ESI† and from the Cambridge Crystallographic Data Center (www.ccdc.cam.ac.uk). CCDC reference number: Cr(TMP)Cl•H$_2$O (1001312), 2 (999173), 10 (1000580), 12 (999100).

2.5.3 Synthesis of chromium porphyrins

_Free base porphyrin ligands_ H$_2$(P), (P = TPP, TMP, TFP, TNAP, TFMP) were prepared following the method of Gonsalves et al.$^{83}$ and Sun et al.$^{84}$ with several modifications. In particular, nitrotoluene was used in place of nitrobenzene. A solution of glacial acetic acid (90 mL), propionic acid (45 mL) and nitrotoluene (60 mL) was prepared in a 500 mL three-neck-round-bottom flask which was equipped with a reflux condenser and two 100 mL dropping
funnels. One of the dropping funnels was charged with the corresponding benzaldehyde (30 mmol, dissolved in 60 mL nitrotoluene), and the other addition funnel was charged with freshly distilled pyrrole (2.09 mL, 30 mmol, dissolved in 45 mL propionic acid). After heating the nitrotoluene mixture to 110 °C, the corresponding benzaldehyde and pyrrole were added slowly to this solution, resulting in a final ratio of glacial acetic acid: propionic acid: nitrotoluene of 3:3:4. After refluxing for an additional 3 h, the black solution was cooled to room temperature, transferred to an Erlenmeyer flask and further cooled to -15 °C for 1 h. The resulting purple-pink crystalline solid was then collected and washed with methanol until the filtrate was clear. The final product was then dried at 80 °C under reduced pressure. This column chromatography-free method affords free base porphyrin in reasonable yield. H$_2$TPP$^{85}$ (Yield: 0.70 g, 15%), H$_2$TMP$^{85}$ (Yield: 1.17 g, 21%), H$_2$TFP$^{85}$ (Yield: 2.08 g, 40%), H$_2$TNAP$^{86}$ (Yield: 0.75 g, 12%), and H$_2$TFMP$^{87}$ (Yield: 1.76 g, 26%) have been previously reported. All spectra are consistent with previous reports.$^{85-87}$

*Chromium porphyrin metallation*, The metallation procedures of Groves$^{88}$ was followed with minor modification. In a 500 mL three-neck-round-bottom flask equipped with a reflux condenser, the corresponding porphyrin (1.6 mmol) was dissolved in 150 mL dimethylformamide. After the solution was heated to reflux, anhydrous CrCl$_2$ (ca: 0.5~1 g, 3.2~6.4 mmol) was separated into 5 portions and added to the solution every 10 min under N$_2$ atmosphere. Reaction progress was monitored by UV/Vis until all free base porphyrin was consumed. The solution was then cooled to room temperature and transferred to an Erlenmeyer flask. A 150 mL saturated NaCl solution was added and this was stored at -15 °C overnight. The resulting purple crystalline solid was collected on Celite. This was subsequently washed with 200 mL deionized water, 200 mL hexane and finally extracted with 200 mL
dichloromethane. After removal of dichloromethane, the product was dried under vacuum at 80 °C for 1 h. Cr(PPP)Cl\textsuperscript{84} (Yield: 0.99 g, 89%), Cr(TMP)Cl\textsuperscript{88} (Yield: 1.27 g, 97%), Cr(TFP)Cl\textsuperscript{45} (Yield: 1.23 g, 99%) and Cr(TFMP)Cl\textsuperscript{45} (Yield: 1.41 g, 91%) have been reported previously. All spectra of the above compounds are consistent with previous reports.\textsuperscript{45,54,88}

Yield of Cr(TNAP)Cl: 1.42 g, 99%, UV/Vis (CH\textsubscript{2}Cl\textsubscript{2}), \(\lambda_{\text{max}}\) (nm) (\(\varepsilon\) (M\(^{-1}\)cm\(^{-1}\))), 395(3160), 454(17000), 524(6600), 567(10200), 605(7400), 635(7400), HRMS-ESI (M\(^+\)): calc’d for C\textsubscript{60}H\textsubscript{36}CrN\textsubscript{8} 864.2340, found: 864.2316

2.5.4 Synthesis of (tmtaa)Ti═O→Cr(Por)Cl binuclear complexes

(tmtaa)Ti═O→Cr(PPP)Cl, (1). In the glovebox, (tmtaa)Ti═O (50.0 mg, 0.12 mmol) and Cr(PPP)Cl (86.0 mg 0.12 mmol) were added to 12 mL of a 1:1 acetonitrile:toluene mixture in a 50 mL Teflon-sealed Schlenk flask and heated at 80 °C for 12 h. The solution was then cooled slowly to room temperature and was filtered to remove the side products [Ti═O→Cr←O═Ti]\textsuperscript{+} trimer (compound 4) and [Ti−O−Ti]\textsuperscript{2+} (the dimerization product of (tmtaa)Ti═O).\textsuperscript{32,33} A fine green powder was obtained from the filtrate after removal of the solvent in vacuo. The final product was obtained after recrystallization via layered diffusion of pentane (15 mL) into a dichloromethane (3 mL) solution at -25 °C. Yield after recrystallization: 99.8 mg, 73%, UV/Vis (CH\textsubscript{2}Cl\textsubscript{2}) \(\lambda_{\text{max}}\) (nm) (\(\varepsilon\) (M\(^{-1}\)cm\(^{-1}\))), 345 (44400), 396 (51800), 430 (31400), 452 (115500), 526 (5400), 581 (8600), 618 (14000), 634 (8000), ATR/FT-IR \(\nu_{\text{Ti=O}}\) (cm\(^{-1}\)): 903(s). Anal. calc’d for C\textsubscript{66}H\textsubscript{50}ClCrN\textsubscript{8}OTi•0.5CH\textsubscript{2}Cl\textsubscript{2}: C, 69.52; H, 4.47; N, 9.75. Found: C, 70.27; H, 4.52; N, 9.66. HRMS-ESI (M\(^+\)) calc’d for C\textsubscript{66}H\textsubscript{50}CrN\textsubscript{8}OTi: 1070.2987. Found 1070.2978. \(\mu_{\text{eff}}\) (\(\mu\text{B}\))(CDCl\textsubscript{3}): 3.87.

(tmtaa)Ti═O→Cr(TMP)Cl, (2). The compound was synthesized and purified by following a procedure similar to that described above for 1 using Cr(TMP)Cl (101.0 mg 0.12 mmol),
(tmtaa)Ti═O (50.0 mg, 0.12 mmol) and 12 mL 1:1 acetonitrile:toluene mixture. X-ray quality crystals were obtained via vapor diffusion of pentane into a solution of 6 mg of this solid in 0.5 mL dichloromethane. Yield after recrystallization: 74.9 mg, 50%. UV/Vis (CH$_2$Cl$_2$), $\lambda_{\text{max}}$ (nm) ($\varepsilon$ (M$^{-1}$cm$^{-1}$)), 340(54600), 396(64800), 454(182600), 524(7500), 572(12300), 612(15700). ATR/FT-IR $\nu_{\text{Ti=O}}$ (cm$^{-1}$): 903. Anal. calc’d for C$_{70}$H$_{58}$ClCrN$_8$O$_5$Ti•1CH$_2$Cl$_2$: C, 65.02; H, 4.61; N, 8.54. Found: C, 65.19; H, 4.71; N, 8.75. HRMS-ESI (M$^+$) calc’d for C$_{70}$H$_{58}$CrN$_8$O$_5$Ti: 1190.3409. Found: 1190.3389. $\mu_{\text{eff}}$($\mu_B$)(CDCl$_3$): 3.70

(tmtaa)Ti═O$\rightarrow$Cr(TNAP)Cl, (3). The compound was synthesized by following a procedure similar to that described above for 1 using Cr(TNAP)Cl (110.8 mg 0.12 mmol), (tmtaa)Ti═O (50.0 mg, 0.12 mmol) and 5 mL 1:1 acetonitrile:toluene mixture. Crude 3 can be obtained as a precipitate when cooled to room temperature. The resulting solid was purified similarly to 1. Yield after recrystallization: 114.0 mg, 71%. UV/Vis (CH$_2$Cl$_2$), $\lambda_{\text{max}}$ (nm)($\varepsilon$ (M$^{-1}$cm$^{-1}$)), 346 (63100), 395 (71900), 458 (158700), 525 (13000), 575 (14900), 623 (176004), 640 (13200). ATR/FT-IR $\nu_{\text{Ti=O}}$ (cm$^{-1}$): 916. Anal. calc’d for C$_{82}$H$_{58}$ClCrN$_8$O$_5$Ti•0.5CH$_2$Cl$_2$: C, 73.12; H, 4.83; N, 8.27. Found: C, 73.42; H, 4.88; N, 8.53. HRMS-ESI (M$^+$) calc’d for C$_{82}$H$_{58}$CrN$_8$OTi: 1270.3613. Found: 1270.3622. $\mu_{\text{eff}}$($\mu_B$)(CDCl$_3$): 3.61.

2.5.5 Synthesis of [(tmtaa)Ti═O$\rightarrow$Cr(Por)$\leftarrow$O═Ti(tmtaa)]$^+$ trinuclear complexes

[(tmtaa)Ti═O$\rightarrow$Cr(PP)$\leftarrow$O═Ti(tmtaa)]Cl, (4). The compound was synthesized by following a procedure similar to that described above for 1 using (tmtaa)Ti═O (50.0 mg, 0.12 mmol), Cr (TPP)Cl (43.0 mg 0.062 mmol) and 5 mL 1:1 acetonitrile:toluene mixture. After reaction, solid 4 was collected out of this mixture by filtration. The resulting solid was purified similarly to 1. Yield after recrystallization: 52.3 mg, 56%, UV/Vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ (nm)($\varepsilon$ (M$^{-1}$cm$^{-1}$)): 344 (75300), 390 (83000), 423 (38600), 456 (79800), 527 (4700), 582 (6800), 616
(9200), 636 (5700). ATR/FT-IR $\nu_{\text{Ti}=\text{O}}$ (cm$^{-1}$): 901(s). Anal. calc'd for C$_{88}$H$_{72}$ClCrN$_{12}$O$_2$Ti$_2$•1CH$_2$Cl$_2$: C, 66.91; H, 4.67; N, 10.52. Found: C, 66.16; H, 4.64; N, 10.96. HRMS-ESI (M$^+$) calc'd for C$_{88}$H$_{72}$CrN$_{12}$O$_2$Ti$_2$: 1476.4260. Found 1476.4279. $\mu_{\text{eff}}$ ($\mu_\text{B}$)(CDCl$_3$): 3.39.

[(tmtaa)Ti=O→Cr(TMP)←O=Ti(tmtaa)]Cl, (5). The compound was synthesized and purified by following a procedure similar to that described above for 4 using Cr(TMP)Cl (50.5 mg 0.062 mmol), (tmtaa)Ti=O (50.0 mg, 0.12 mmol) and 5 mL 1:1 acetonitrile:toluene mixture. Yield after recrystallization: 65.7 mg, 65%. UV/Vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ (nm) ($\varepsilon$ (M$^{-1}$cm$^{-1}$)): 346 (70300), 390 (89000), 423 (31700), 458 (98000), 533 (4600), 586 (7100), 620 (14300), 636(12400). ATR/FT-IR $\nu_{\text{Ti}=\text{O}}$ (cm$^{-1}$): 900(s). Anal. calc'd for C$_{92}$H$_{80}$ClCrN$_{12}$O$_6$Ti$_2$: C, 65.02; H, 4.81; N, 9.78. Found: C, 64.94; H, 4.77; N, 9.97. HRMS-ESI (M$^+$) calc'd for C$_{92}$H$_{80}$CrN$_{12}$O$_6$Ti$_2$: 1596.4682. Found 1596.4702. $\mu_{\text{eff}}$ ($\mu_\text{B}$)(CDCl$_3$): 3.70.

[(tmtaa)Ti=O→Cr(TFP)←O=Ti(tmtaa)]Cl, (6). The compound was synthesized and purified by following a procedure similar to that described above for 4 using Cr(TFP)Cl (47.5 mg 0.062 mol), (tmtaa)Ti=O (50.0 mg, 0.12 mmol) and 5 mL 1:1 acetonitrile:toluene mixture. Yield after recrystallization: 47.0 mg, 48%. UV/Vis (CH$_2$Cl$_2$), $\lambda_{\text{max}}$ (nm) ($\varepsilon$ (M$^{-1}$cm$^{-1}$)): 341 (71600), 391 (77400) 417 (47200) 455 (86000) 525 (6200), 579 (90000) 616 (11300) 636 (7700). ATR/FT-IR $\nu_{\text{Ti}=\text{O}}$ (cm$^{-1}$): 901(s). Anal. calc'd for C$_{88}$H$_{68}$ClCrF$_4$N$_{12}$O$_2$Ti$_2$•5CH$_2$Cl$_2$: C, 55.59; H, 3.91; N, 8.36. Found: C, 55.94; H, 4.16; N, 8.41. HRMS-ESI (M$^+$) calc'd for C$_{88}$H$_{68}$CrF$_4$N$_{12}$O$_2$Ti$_2$: 1548.3883. Found. 1548.3857 $\mu_{\text{eff}}$ ($\mu_\text{B}$) (CD$_2$Cl$_2$): 3.20.

[(tmtaa)Ti=O→Cr(TFMP)←O=Ti(tmtaa)]Cl, (7). The compound was synthesized and purified by following a procedure similar to that described above for 4 using Cr(TFMP)Cl (47.5 mg 0.062 mmol), (tmtaa)Ti=O (50.0 mg, 0.12 mmol) and 3 mL 1:1 acetonitrile:toluene
mixture. Yield after recrystallization: 45.0 mg, 46%, UV/Vis (CH$_2$Cl$_2$), $\lambda_{\text{max}}$ (nm) ($\varepsilon$ (M$^{-1}$cm$^{-1}$)), 341(80700), 392(81100), 425(39400), 454(95100), 529(4200), 576(8500), 613(9600).

ATR/FT-IR $\nu_{\text{Ti}=\text{O}}$ (cm$^{-1}$): 899(s). Anal. calc'd for C$_{92}$H$_{68}$ClCrF$_{12}$N$_{12}$O$_2$Ti$_2$: C, 60.80; H, 3.81; N, 9.20. Found: C, 59.96; H, 3.93; N, 9.21. HRMS-ESI (M$^+$) calc'd for C$_{92}$H$_{68}$ClCrF$_{12}$N$_{12}$O$_2$Ti$_2$: 1748.3755. Found: 1748.3729. $\mu_{\text{eff}}$ (\mu_B) (CD$_2$Cl$_2$): 3.82.

$[(\text{tmtaa})\text{Ti}=\text{O}\rightarrow\text{Cr(TPP)}\leftarrow\text{O}=\text{Ti(\text{tmtaa})}]\text{SbF}_6$ (8). The compound was synthesized and purified by following a procedure similar to that described above for 4. Using (tmtaa)Ti=O (50.0 mg, 0.12 mmol), Cr(TPP)Cl (43.1 mg, 0.062 mmol), NaSbF$_6$ (17.5 mg, 0.068 mmol) and 8 mL 1:1 acetonitrile:toluene mixture. Yield after recrystallization: 54.2 mg, 53%, UV/Vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ (nm) ($\varepsilon$ (M$^{-1}$cm$^{-1}$)), 345(44200), 390(52700), 424(22900), 456 (56400), 530(3200), 585(4700), 621(8100), 635(7200). ATR/FT-IR $\nu_{\text{Ti}=\text{O}}$ (cm$^{-1}$): 900(s), $\nu_{\text{Sb-F}}$ (cm$^{-1}$): 653, Anal. calc'd for C$_{88}$H$_{72}$CrF$_6$N$_{12}$O$_2$SbTi$_2$: C, 59.45; H, 4.15; N, 9.35. Found: C, 58.66; H, 4.05; N, 9.68. HRMS-ESI (M$^+$) calc'd for C$_{88}$H$_{72}$CrN$_{12}$O$_2$Ti$_2$: 1476.4260. Found 1476.4258. $\mu_{\text{eff}}$ (\mu_B) (CDCl$_3$): 3.30.

$[(\text{tmtaa})\text{Ti}=\text{O}\rightarrow\text{Cr(TMPP)}\leftarrow\text{O}=\text{Ti(\text{tmtaa})}]\text{SbF}_6$ (9). The compound was synthesized and purified by following a procedure similar to that described above for 4 using Cr(TMPP)Cl (50.5 mg 0.062 mol), (tmtaa)Ti=O (50.0 mg, 0.12 mmol), NaSbF$_6$ (17.5 mg, 0.068 mmol) and 8 mL 1:1 acetonitrile:toluene mixture. Yield after recrystallization: 48.7 mg, 44%, UV/Vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ (nm) ($\varepsilon$ (M$^{-1}$cm$^{-1}$)), 345(48600), 391(59400), 422(26200), 459(59300), 531(3700), 585(5500), 620(9000), 635(6800). ATR/FT-IR $\nu_{\text{Ti}=\text{O}}$ (cm$^{-1}$): 909(s), $\nu_{\text{Sb-F}}$ (cm$^{-1}$): 658cm$^{-1}$, Anal. calc'd for C$_{92}$H$_{80}$CrF$_6$N$_{12}$O$_6$SbTi$_2$: C, 53.06; H, 4.08; N, 7.74. Found: C, 52.88; H, 4.13; N, 7.97. HRMS-ESI (M$^+$) calc'd for C$_{92}$H$_{80}$CrN$_{12}$O$_6$Ti$_2$: 1596.4682. Found 1596.4670. $\mu_{\text{eff}}$ (\mu_B)(CDCl$_3$): 3.03.
[(tmtaa)Ti═O→Cr(TFP)←O═Ti(tmtaa)]SbF$_6$ (10). The compound was synthesized and purified by following a procedure similar to that described above for 4 using Cr(TFP)Cl (47.5 mg 0.062 mmol), (tmtaa)Ti═O (50.0 mg, 0.12 mmol), NaSbF$_6$ (17.5 mg, 0.068 mmol) and 8 mL 1:1 acetonitrile:toluene mixture. X-ray quality crystals were prepared similarly to 2. Yield after recrystallization: 42.9 mg, 40%, UV/Vis (CH$_2$Cl$_2$) $\lambda_{max}$ (nm) (ε (M$^{-1}$cm$^{-1}$)), 347(54181), 391(58700), 424(32000), 454(62400), 526(5400), 577(7000), 613(8400), 635(6300). Anal. calc’d for C$_{88}$H$_{68}$CrF$_{10}$N$_{12}$O$_2$SbTi$_2$•4CH$_2$Cl$_2$: C, 52.01; H, 3.61; N, 8.94. Found: C, 52.04; H, 3.54; N, 8.77. ATR/FT-IR ν$_{Ti=O}$ (cm$^{-1}$): 894(s), ν$_{Sb-F}$ (cm$^{-1}$): 654cm$^{-1}$. HRMS-ESI (M$^+$) calc’d for C$_{88}$H$_{68}$CrF$_{10}$N$_{12}$O$_2$Ti$_2$: 1548.3883. Found: 1548.3857. μ$_{eff}$ (μ$_B$)(CD$_2$Cl$_2$): 3.37

[(tmtaa)Ti═O→Cr(TFMP)←O═Ti(tmtaa)]SbF$_6$ (11). The compound was synthesized by following a procedure similar to that described above for 4 using Cr(TFMP)Cl (60.3 mg 0.062 mmol). (tmtaa)Ti═O (50.0 mg, 0.12 mmol), NaSbF$_6$ (17.5 mg, 0.068 mmol) and 3 mL 1:1 acetonitrile:toluene mixture. Yield after recrystallization: 43.5 mg, 37%, UV/Vis (CH$_2$Cl$_2$) $\lambda_{max}$ (nm) (ε (M$^{-1}$cm$^{-1}$)), 347(60700), 391(60000), 424(33000), 454(66000), 527(3700), 578(5800), 612(6100). ATR/FT-IR ν$_{Ti=O}$ (cm$^{-1}$): 906(s), ν$_{Sb-F}$ (cm$^{-1}$): 657cm$^{-1}$. Anal. calc’d for C$_{92}$H$_{68}$CrF$_{18}$N$_{12}$O$_2$Ti$_2$•4CH$_2$Cl$_2$: C, 49.60; H, 3.30; N, 7.23. Found: C, 49.13; H, 3.63; N, 6.53. HRMS-ESI (M$^+$) calc’d for C$_{92}$H$_{68}$CrF$_{18}$N$_{12}$O$_2$Ti$_2$: 1748.3755. Found: 1748.3729. HRMS-ESI (M$^+$) calc’d for SbF$_6$: 234.8948. Found: 234.8938. μ$_{eff}$ (μ$_B$)(CD$_2$Cl$_2$): 3.11

[(tmtaa)Ti═O→Cr(TFMP)←O═Ti(tmtaa)][ClH$_4$TFMP] (12). The compound was synthesized by following a procedure similar to that described above for 4 using 7 (25 mg 0.014 mmol), H$_4$TFMP (18.7 mg 0.021 mmol), (tmtaa)Ti═O (5.7 mg, 0.014 mmol) and 8 mL 1:1 acetonitrile:toluene mixture. Pure material was obtained as orange plates after slow cooling.
of the mixture. Crude yield: 9.1 mg, 25%. UV/Vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ (nm), 343, 392, 425, 455, 529, 577, 611. ATR/FT-IR $\nu_{\text{Ti=O}}$ (cm$^{-1}$): 906(s). HRMS-ESI (M$^+$) calc’d for C$_{92}$H$_{68}$CrF$_{12}$N$_{12}$O$_2$Ti$_2$: 1748.3755. Found: 1748.3762. HRMS-ESI (M$^-$) calc’d for C$_{48}$H$_{32}$ClF$_{12}$N$_4$: 927.2129. Found: 927.2141.

2.6 Supporting information

The SI contains synthetic details for the anion trap (H$_4$TFMP), details of the titration experiments and use of the Hills equation, electrochemical details, X-ray crystallographic information, details of the SQUID experiment, solid state ATR-FT-IR spectrum and molar extinction coefficients of 1-12.

Synthetic detail for the anion trap, the porphyrinogen H$_4$TFMP

Synthesis of 5,10,15,20-tetrakis((4-trifluoromethyl)phenyl) porphyrinogen (H$_4$TFMP, Scheme 2.51) follows the previously reported method of Lindsey. Under the protection of N$_2$, freshly distilled pyrrole (0.35 mL, 0.01 M) and 4-trifluoromethyl benzaldehyde (0.69 mL, 0.01 M) were dissolved in 500 mL dichloromethane. After stirring for 5 min, trifluoroacetic acid (0.38 mL, 0.01 M) was added. The reaction was further stirred for 3 hours under room temperature at which time the solvent was removed under a vacuum. The black residue was transferred to a column with silica gel. Elution with dichloromethane: petroleum ether (6:4) affords the porphyrinogen (0.088 g, 7.3%) as the first fraction. The $^1$H NMR is similar to porphyrinogens with other substituents as previously reported by Dolphin. $^1$H NMR (400 MHz, CDCl$_3$): 7.89~7.81 (N-H, m, 8H), 7.59 (meta-phenyl, d, 2H, $J = 8$ Hz), 7.34 (o-phenyl, d, 8H, $J = 8$ Hz), 5.79~5.73 ($\beta$-pyrrole md, 8H, $J = 2.8$ Hz), 5.48 (meso-H, s, 4H).

$^{13}$C NMR (400 MHz, CD$_2$Cl$_2$): 145.65, 132.00, 128.83, 128.66, 125.64, 108.37, 44.05.
$^{19}$F NMR (376 MHz, CDCl3): -80.5 (bs)

Scheme 2.S1. Molecular scheme for the 5,10,15,20-tetrakis((4-trifluoromethyl)phenyl) porphyrinogen.

Details of the titration experiment

A titration experiment was performed following the procedure of Hoffman and coworkers. The Hills equation, below, was used to determine reaction stoichiometry. ($Y = [C]/[C]_0$, $[L]$: concentration of unbounded ligand) The results are discussed in the text of the manuscript.

$$\log \left(\frac{Y}{1-Y}\right) = n \log [L] + K_a$$
Figure 2.S1. Visible spectral changes upon the addition of (tmtaa)Ti═O to $3.21 \times 10^{-5}$ M Cr(TPP)Cl in dichloromethane at 298 K. The concentration of (tmtaa)Ti═O from 1 to 10 are ($\times 10^{-4}$) 0.24, 0.48, 0.72, 0.95, 1.17, 1.39, 1.61, 1.82, 2.03, 2.24 M, respectively.
a. \( \text{Cr(TPP)Cl} + (\text{tmtaa})\text{Ti} \equiv \text{O} \)

\[
y = 1.0364x + 3.7178 \\
R^2 = 0.9968
\]

b. \( \text{Cr(TNAP)Cl} + (\text{tmtaa})\text{Ti} \equiv \text{O} \)

\[
y = 1.0313x + 3.312 \\
R^2 = 0.9962
\]
**Figure 2.S2.** a. Cr(TPP)Cl solution titrated with (tmtaa)Ti═O; b. Cr(TNAP)Cl titrated with (tmtaa)Ti═O; c. 1 titrated with (tmtaa)Ti═O. The change of absorbance at 619 nm (for $K_1$) and 474 nm (for $K_2$) are used to fit into Hill’s equation: $\ln \left( \frac{Y}{1-Y} \right) = n \ln[L] + K_a$, where $\ln[L]$ is set to X axis and $\ln \left( \frac{Y}{1-Y} \right)$ is set to Y axis. In c, the curve is not perfectly linear, presumably due to the isomerization between heterobimetallic compound 1 and heterotrimetallic compound 4 as observed from electrochemistry.

**Figure 2.S3.** Possible atropisomers of compound 3 from the thermal rotation of the naphthyl rings. For (a) and (b) the naphthyl rings have point-up direction that may prevent the binding of a second equivalent of (tmtaa)Ti═O. Although the atropisomer (c) has no steric interference for an incoming (tmtaa)Ti═O, the naphthyl point-down geometry makes this atropisomer
unlikely to be significantly present in solution. In a summary, the directional steric bulk of the naphthyl substituents appear to prevent the addition of another equivalent of (tmtaa)Ti═O, explaining our observations that the bimetallic 3 does not react to form a trimetallic compound.

**Electrochemical Details**

Cyclic voltammograms for (tmtaa)Ti═O, Cr(TMP)Cl•H2O compound 1, 3-7, 9-11 are depicted in Figure 2.S4-S7. At 50 mV/s scan rate, the trimetallic compounds typically have one quasi-reversible peak at -1.83 V (ΔE = 0.228 V) versus to Fc/Fc⁺. When higher scan rate is applied, this quasi-reversible peak will convert into two very close reversible peaks -1.73 V (ΔE = 0.098 V) and -1.88 V (ΔE = 0.100 V)). In contrast to the trimetallic compound 5, bimetallic compounds 1 and 3 have only one reversible peak at around -1.70 V (ΔE = 0.135 V), but are irreversible at ~ -1.89 V. Since titration experiments indicate that a second (tmtaa)Ti═O can be added to bimetallic compound 1, in order to avoid the interference of trimetallic impurities 3 was used as a control. As shown in Figure 2.S7, the cyclic voltammetry spectrum of compound 3 still has one reversible and one irreversible peak.

The different electrochemical behavior of bimetallic and trimetallic complexes can be explained via the square mechanism shown in Figure 2.S8. At fast scan rates (> 200 mV/s), two reaction paths way are observed when external potential is applied to [(tmtaa)Ti═O→CrIII(Por)←O═Ti(tmtaa)]Cl. In first path (process I in Figure 2.S8), a direct reduction occurs to form [(tmtaa)Ti═O→CrIII(Por*)←O═Ti(tmtaa)]Cl. This species is then in equilibrium with bimetallic [(tmtaa)Ti═O→CrIII(Por*)−Cl]− after isomerization between chloride and (tmtaa)Ti═O. However, isomerization between chloride and (tmtaa)Ti═O can occur before electron transfer reaction. The resulting bimetallic (tmtaa)Ti═O→CrIII(Por)−Cl will undergo electron transfer in a second path (process II) to form [(tmtaa)Ti═O→CrIII(Por*)−Cl]−. At slower scan rates (<50 mV/s), only one quasi-reversible
peak ($\Delta E = 0.228$ V) is observed. This suggests that electron transfer and ligand isomerization reach equilibrium. This isomerization process is consistent with the observed small second (tmtaa)Ti═O addition equilibrium constant ($\log K_2 = 2.67$).

**Figure 2.S4.** Cyclic voltammetry of (tmtaa)Ti═O, Cr(TMP)Cl·H$_2$O, complex 9 in degassed, dry dichloromethane with 0.1 M tetrabutylammonium hexafluorophosphate using glassy carbon working electrode, platinum counter electrode and silver wire quasi reference electrode. All signals were referenced to ferrocene/ferrocenium (Fc/Fc$^+$) at 0 V. The labeled currents are the redox process suggested as following: a, Cr$^{III}$ - e$^-$$\rightarrow$Cr$^{IV}$; b, Cr$^{IV}$Por - e$^-$$\rightarrow$Cr$^{IV}$Por$^+$; c, (tmtaa)Ti═O - e$^-$$\rightarrow$[(tmtaa)Ti═O]$^+$; d, Cr$^{III}$Por + e$^-$$\rightarrow$Cr$^{III}$Por$^+$; Cr$^{III}$Por$^-$ + e$^-$$\rightarrow$ Cr$^{III}$Por$^2$ or Cr$^{III}$Por$^2$. 
Figure 2.5. Cyclic voltammetry of complex 4-7 in degassed, dry dichloromethane with 0.1 M tetrabutylammonium hexafluorophosphate using glassy carbon working electrode, platinum counter electrode and silver wire quasi reference electrode. All signals were referenced to ferrocene/ferrocnium($\text{Fc/Fc}^+$) at 0 V.
Figure 2.S6. Cyclic voltammetry of complex 9-11 in degassed, dry dichloromethane with 0.1 M tetrabutylammonium hexafluorophosphate using glassy carbon working electrode, platinum counter electrode and silver wire quasi reference electrode. All signals were referenced to ferrocene/ferrocinium(Fc/Fc⁺) at 0 V.
Figure 2.S7. Cyclic voltammetry of complex 1 and 3 in degassed, dry dichloromethane with 0.1 M tetrabutylammonium hexafluorophosphate using glassy carbon working electrode,
platinum counter electrode and silver wire quasi reference electrode. All signals were referenced to ferrocene/ferrocenium (Fc/Fc\textsuperscript{+}) at 0 V.

\[
\text{(tmtaa)Ti=O} \rightarrow \text{Cr}^{III}(\text{Por}) \leftrightarrow \text{O=Ti(tmtaa)}\]

\[
\text{I} \quad \begin{array}{c}
\text{e}^- \\
\text{-e}^-
\end{array}
\]

\[
\text{(tmtaa)Ti=O} \rightarrow \text{Cr}^{III}(\text{Por}^{+}) \leftrightarrow \text{O=Ti(tmtaa)}
\]

\[
+ \text{(tmtaa)Ti}=\text{O} \quad \quad - \text{(tmtaa)Ti}=\text{O}
\]

\[
- \text{Cl}^- \quad \quad + \text{Cl}^-
\]

\[
\text{II} \quad \begin{array}{c}
\text{e}^- \\
\text{-e}^-
\end{array}
\]

\[
- \text{(tmtaa)Ti}=\text{O} \quad \quad + \text{Cl}^-
\]

\[
\text{(tmtaa)Ti}=\text{O} \rightarrow \text{Cr}^{III}(\text{Por}) \rightarrow \text{Cl}
\]

\[
\text{e}^- \\
\text{-e}^-
\]

\[
\text{(tmtaa)Ti}=\text{O} \rightarrow \text{Cr}^{III}(\text{Por}^{+}) \rightarrow \text{Cl}^-\]

**Figure 2.S8.** Square mechanism adopted from previous work that describes the different reduction behavior of the bimetallic and trimetallic compounds. Process I and II stand for two reversible redox processes at 1.73 V (\( \Delta E = 0.098 V \)) and 1.88 V (\( \Delta E = 0.100V \)) respectively;

Crystallography

**Figure 2.S9.** Numbered molecular structure of Cr(TMP)Cl\textbullet H\textsubscript{2}O. Thermal ellipsoids drawn at 50% probability. Hydrogen atoms (except bridging hydrogen from H\textsubscript{2}O at axial position) and solvent molecules are omitted for clarity.
A dark black plate-like specimen of C₅₄H₄₇N₇O₅ClCr, approximate dimensions 0.097 mm × 0.200 mm × 0.280 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

A total of 1513 frames were collected. The total exposure time was 26.73 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 38323 reflections to a maximum θ angle of 28.282° (0.75 Å resolution), of which 11094 were independent (average redundancy 3.45, completeness = 92.3 %, Rint = 5.22%, Rsig = 5.11%) and 10147 (91.46%) were greater than 2σ(F²). The final cell constants of a = 14.8022(6) Å, b = 9.1685(4) Å, c = 18.1960(7) Å, α = 90°, β = 99.490(2)°, γ = 90°, volume = 2435.66(17) Å³, are based upon the refinement of the XYZ-centroids of 9979 reflections above 20 σ(I) with 4.538° < 2θ < 56.320°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.7377.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P n, with Z = 2 for the formula unit, C₅₄H₄₇N₇O₅ClCr. The final anisotropic full-matrix least-squares refinement on F² with 621 variables converged at R₁ = 4.79%, for the observed data and wR² = 12.74% for all data. The goodness-of-fit was 1.046. The largest peak in the final difference electron density synthesis was 0.503 e-/Å³ and the largest hole was -0.361 e-/Å³ with an RMS deviation of 0.067 e-/Å³. On the basis of the final model, the calculated density was 1.311 g/cm³ and F(000), 1002 e⁻.
Figure 2. S10. Numbered molecular structure of 2. Thermal ellipsoids drawn at 50% probability. Hydrogen atoms and solvent molecules are omitted for clarity.

A dark black plate-like specimen of C\textsubscript{72}H\textsubscript{62}Cl\textsubscript{5}CrN\textsubscript{8}O\textsubscript{5}Ti, approximate dimensions 0.174 mm × 0.285 mm × 0.876 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

A total of 1691 frames were collected. The total exposure time was 14.93 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 140213 reflections to a maximum θ angle of 31.428° (0.68 Å resolution), of which 20785 were independent (average redundancy 6.75, completeness = 100.0 %, Rint = 3.38%, Rsig = 2.59%) and 18893 (77.07%) were greater than 2σ(F\textsuperscript{2}). The final cell constants of a = 16.0177(7) Å, b = 19.5409(8) Å, c = 20.1114(9) Å, volume = 6294.9(5) Å\textsuperscript{3}, are based upon the refinement of the XYZ-
centroids of 9511 reflections above 20σ(I) with 4.556° < 2θ < 62.764°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.8645.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P2₁2₁2₁, with Z = 4 for the formula unit, C₇₂H₆₂Cl₅CrN₆O₅Ti. The final anisotropic full-matrix least-squares refinement on F² with 883 variables converged at R₁ = 3.47 %, for the observed data and wR₂ = 9.36 % for all data. The goodness-of-fit was 1.043. The largest peak in the final difference electron density synthesis was 0.775 e-/Å³ and the largest hole was -0.538 e-/Å³ with an RMS deviation of 0.067 e-/Å³. On the basis of the final model, the calculated density was 1.473 g/cm³ and F(000), 2884.0 e⁻.

Figure 2.S11. Numbered molecular structure of 10. Thermal ellipsoids drawn at 50% probability. Hydrogen atoms, anion and solvent molecules are omitted for clarity.
A dark black plate-like specimen of C_{88}H_{68}CrF_{10}N_{12}O_{2}SbTi_{2}, approximate dimensions 0.345 mm × 0.299 mm × 0.151 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

A total of 1412 frames were collected. The total exposure time was 21.76 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 135401 reflections to a maximum θ angle of 27.047° (0.78 Å resolution), of which 19818 were independent (average redundancy 6.83, completeness = 99.8%, Rint = 4.26%, Rsig = 3.07%) and 15256 (76.98%) were greater than 2σ(F2). The final cell constants of a = 16.0036(8) Å, b = 24.1922(10) Å, c = 23.4013(12) Å, α = 90°, β = 92.667(2)°, γ = 90°, volume = 9050.3(7) Å³, are based upon the refinement of the XYZ-centroids of 9265 reflections above 20 σ(I) with 4.522° < 2θ < 53.860°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.8891.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P12_1/n1, with Z = 4 for the formula unit, C_{88}H_{68}CrF_{10}N_{12}O_{2}SbTi_{2}. The final anisotropic full-matrix least-squares refinement on F2 with 1041 variables converged at R1 = 6.79%, for the observed data and wR2 = 16.78% for all data. The goodness-of-fit was 1.057. The largest peak in the final difference electron density synthesis was 1.978 e-/Å³ and the largest hole was -3.501 e-/Å³ with an RMS deviation of 0.098 e-/Å³. On the basis of the final model, the calculated density was 1.310 g/cm³ and F(000), 3620 e⁻.
Figure 2.S12. Single-crystal X-ray structure of trimetallic complex 12. Thermal ellipsoids drawn at 50% probability. Hydrogen atoms (except for hydrogen bonding) and solvent molecules are omitted for clarity.

A dark black plate-like specimen of C\textsubscript{150}H\textsubscript{115}ClCrF\textsubscript{24}N\textsubscript{21}O\textsubscript{2}Ti\textsubscript{2}, approximate dimensions 0.120 mm × 0.200 mm × 0.260 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

A total of 960 frames were collected. The total exposure time was 23.07 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a tetragonal unit cell yielded a total of 72806 reflections to a maximum θ angle of 29.58° (0.72 Å resolution), of which 9429 were independent (average redundancy 7.721, completeness = 99.6 %, R\text{int} = 2.93%, R\text{sig} = 2.07%) and 7343 (77.88%) were greater than 2σ(F\textsuperscript{2}). The final cell constants of a = 23.1810(7) Å, b = 23.1810(7) Å, c = 12.5405(4) Å, volume = 6738.7(5) Å\textsuperscript{3}, are based upon the refinement of the XYZ-centroids of 9847 reflections above 20 σ(I) with 4.785° < 20 < 58.68°. Data were corrected for absorption
effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.889.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 4/n, with Z = 2 for the formula unit, C_{150}H_{115}ClCrF_{24}N_{21}O_{2}Ti_{2}. The final anisotropic full-matrix least-squares refinement on F^2 with 487 variables converged at R_1 = 4.35%, for the observed data and wR_2 = 12.63% for all data. The goodness-of-fit was 1.042. The largest peak in the final difference electron density synthesis was 0.569 e-/Å^3 and the largest hole was -0.576 e-/Å^3 with an RMS deviation of 0.059 e-/Å^3. On the basis of the final model, the calculated density was 1.421 g/cm^3 and F(000), 2958 e^-.

Details of the SQUID experiment

![Graph](image.png)

**Figure 2.S13.** Saturation plot of 8, T = 2 K. Applied filed varied from 0-70000 oe.
Figure 2.S14. \( \chi \)-T plot of 8.
Solid state ATR-FT-IR spectrum and Molar extinction coefficients of 1-12

Figure 2.S15. Solid state ATR-FT-IR spectrum and Molar extinction coefficients of Cr(TNAP)Cl
Figure 2.S16. Solid state ATR-FT-IR spectrum and Molar extinction coefficients of 1
Figure 2.S17. Solid state ATR-FT-IR spectrum and Molar extinction coefficients of 2
Figure 2.S18. Solid state ATR-FT-IR spectrum and Molar extinction coefficients of 3
Figure 2.S19. Solid state ATR-FT-IR spectrum and Molar extinction coefficients of 4
Figure 2.S20. Solid state ATR-FT-IR spectrum and Molar extinction coefficients of 5
Figure 2.S21. Solid state ATR-FT-IR spectrum and Molar extinction coefficients of 6
Figure 2.522. Solid state ATR-FT-IR spectrum and Molar extinction coefficients of 7.
Figure 2.S23. Solid state ATR-FT-IR spectrum and Molar extinction coefficients of 8
Figure 2.S24. Solid state ATR-FT-IR spectrum and Molar extinction coefficients of 9
Figure 2.S25. Solid state ATR-FT-IR spectrum and Molar extinction coefficients of 10
Figure 2.S26. Solid state ATR-FT-IR spectrum and Molar extinction coefficients of 11
Figure 2. Solid state ATR-FT-IR spectrum and Extinction coefficients of 12.
Selected HRMS-ESI result of 2 and 5 and their [M]$^+$ and [M+H]$^+$ simulating patterns.

**Figure 2.S28**, HRMS-ESI result of 2, the top one is experiment result ([M]$^+$ = 1190.33890). Its corresponding simulation pattern of [M]$^+$ and [M+H]$^+$ are shown.

**Figure 2.S29**, HRMS-ESI result of 5, the top one is experiment result ([M]$^+$ = 1596.46699). Its corresponding simulation pattern of [M]$^+$ and [M+H]$^+$ are shown.
Table 2.51 Solid state ATR-FT-IR and molar absorptivity of 1-12 in dichloromethane at 298 K. The representative starting material (tmtaa)Ti═O and Cr(TPP)Cl are listed for comparison

<table>
<thead>
<tr>
<th></th>
<th>(tmtaa)Ti═O based $\lambda_{\text{max}}$, nm (log $\varepsilon$)</th>
<th>Cr$^{\text{III}}$ porphyrin based $\lambda_{\text{max}}$, nm (log $\varepsilon$)</th>
<th>$\nu_{\text{Ti=O}}$ cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[a]</td>
<td>328(4.44), 377(4.64)</td>
<td></td>
<td>920</td>
</tr>
<tr>
<td>[b]</td>
<td></td>
<td>448(5.09), 523(3.71), 565(3.91), 605(3.92), 633(3.83)</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>344(4.64), 396(4.71)</td>
<td>452(5.06), 526(3.73), 581(3.93), 618(4.14), 634(3.91)</td>
<td>903</td>
</tr>
<tr>
<td>2</td>
<td>340(4.73), 396(4.81)</td>
<td>454(5.26), 524(3.87), 572(4.09), 612(4.19)</td>
<td>903</td>
</tr>
<tr>
<td>3</td>
<td>346(4.80), 395(4.86)</td>
<td>458(5.20), 525(4.12), 575(4.17), 623(4.24), 640(4.12)</td>
<td>916</td>
</tr>
<tr>
<td>4</td>
<td>344(4.87), 390(4.91)</td>
<td>456(4.90), 527(3.67), 582(3.83), 616(3.96), 636(3.75)</td>
<td>901</td>
</tr>
<tr>
<td>5</td>
<td>346(4.84), 390(4.95)</td>
<td>458(4.99), 533(3.66), 586(3.85), 620(4.15), 636(4.09)</td>
<td>900</td>
</tr>
<tr>
<td>6</td>
<td>341(4.85), 391(4.89)</td>
<td>455(4.93), 525(3.80), 579(3.96), 616(4.05), 636(3.89)</td>
<td>901</td>
</tr>
<tr>
<td>7</td>
<td>341(4.91), 392(4.91)</td>
<td>454(4.98), 529(3.62), 576(3.93), 613(3.98)</td>
<td>899</td>
</tr>
<tr>
<td>8</td>
<td>345(4.64), 390(4.72)</td>
<td>456(4.75), 530(3.50), 585(3.68), 621(3.91), 635(3.85)</td>
<td>901</td>
</tr>
<tr>
<td>9</td>
<td>345(4.69), 391(4.77)</td>
<td>459(4.77), 531(3.57), 585(3.74), 620(3.95), 635(3.84)</td>
<td>909</td>
</tr>
<tr>
<td>10</td>
<td>347(4.73), 391(4.77)</td>
<td>454(4.80), 526(3.73), 577(3.85), 613(3.92), 635(3.90)</td>
<td>894</td>
</tr>
<tr>
<td>11</td>
<td>347(4.78), 391(4.78)</td>
<td>454(4.82), 527(3.57), 578(3.76), 612(3.78)</td>
<td>906</td>
</tr>
<tr>
<td>12</td>
<td>343, 392</td>
<td>455, 529, 577, 611</td>
<td>902</td>
</tr>
</tbody>
</table>

[a] (tmtaa)Ti═O. [b] Cr(TPP)Cl.
2.7 Acknowledgements

This work was supported by startup funding from North Carolina State University. We acknowledge Xiao Song and Prof. Tatyana Smirnova for assistance in collecting EPR spectra. We acknowledge Daniel Stasiw and Prof. David Shultz for assistance in collecting SQUID data. Mass spectra were obtained at the NCSU Department of Chemistry Mass Spectrometry Facility.

2.8 References


(86) George, R. G.; Padmanabhan, M. *Polyhedron* 2003, 22, 3145.


CHAPTER 3

Ferromagnetic Coupling in d$^1$-d$^3$ Linear Oxido-Bridged Heterometallic Complexes: Ground-State Models of Metal-to-Metal Charge Transfer Excited States

This work was published in Dalton. Trans.


Huang, T performed all general characterization and magnetization work. X-ray diffraction experiment was performed by Huang, T under the instruction of Sommer, R. D. The synthesis was performed by Huang, T, Xu, H. and Wu, X.

Department of Chemistry, North Carolina State University;

Raleigh, NC, 27695-8204
3.1 Abstract

Convenient strategies have been developed to synthesize heterobi/trimetallic oxido complexes containing V(IV)−O−Cr(III), V(IV)−O−Cr(III)−O−Ti(IV) and V(IV)−O−Cr(III)−O−V(IV) cores. These compounds can serve as ground state models for probing the magnetic properties of metal-to-metal charge transfer excited states. Each of these complexes represents the first experimental demonstration of ferromagnetic coupling in a d\(^1\)-d\(^3\) oxido-bridged compound, which confirms a long standing theoretical prediction for such a linkage. Structural characterization reveals a similar structure for each of the bi/trimetallic complexes with identical V=O bond lengths (~1.644 Å) and a linear V−O−Cr geometry. The Cr−O distances (1.943 ~ 1.964 Å) are significantly influenced by the ligands in the trans axial positions. Ferromagnetic coupling between the V(IV) and Cr(III) of V−O−Cr is measured by temperature-dependent magnetic susceptibility, showing \( J = +42.5 \) to \(+50.7 \) cm\(^{-1}\) (\( H = -2J\hat{S}_V \cdot \hat{S}_Cr \)). This is further supported by variable temperature X-band EPR. The values of J are found to be consistent with the function \( J = Ae^{βr} \) (\( A = 9.221 \times 10^8 \) and \( β = 8.607 \) Å\(^{-1}\)), where r is the Cr−O bond distance. We propose a model that links either ferromagnetic or antiferromagnetic exchange coupling with long excited state lifetimes in metal-to-metal charge transfer (MMCT) chromophores.

3.2 Introduction

Molecules with heterometallic cores demonstrate physical and chemical properties that are not observed in their monometallic analogs.\(^1\)-\(^8\) Cooperative effects between two covalently linked metal sites have been extensively explored in cocatalysts,\(^9,10\) single molecule magnets\(^11,12\) and the solid state.\(^13,14\) The unsupported oxido bridged motif\(^6,15,16\) is one of the simplest frameworks among heterometallic complexes and is known to
serve as a structural and functional model for many metalloenzymes and cocatalytic reactions.\textsuperscript{9,12,17} Despite their seemingly simple structure, unsupported oxido bridge complexes remain synthetically challenging targets.\textsuperscript{3,17} with a limited number of structurally characterized examples.\textsuperscript{2,6,15,16,18-23}

Measurement of exchange coupling within oxido-bridged heterobi- and trimetallic complexes is important for fully understanding the magnetic, optical and redox properties of both the ground and excited states.\textsuperscript{13} Among structurally characterized examples, only four include magnetic studies and all possess antiferromagnetic coupling between the metal sites with J values varying from $-18.7$ to $-150$ cm$^{-1}$.\textsuperscript{1,4,16,24} Ferromagnetic exchange coupling is another possible pathway for magnetic coupling in other heterometallic complexes.\textsuperscript{25-27} Empirical, semi-empirical and theoretical calculations have been performed on unsupported oxido-bridged heterobimetallic species, and suggest that moderate ferromagnetic interactions should exist in linear d$^1$-d$^3$ complexes.\textsuperscript{28-30} To our knowledge no experimental data confirming this hypothesis has been reported. Here, we describe three examples of unsupported oxido heterobi- and trimetallic complexes that are ferromagnetically coupled, allowing experimental determination of the properties in such a system for the first time. In addition, we propose that such molecules can serve as ground-state models for probing magnetic and other properties of metal-to-metal charge transfer excited states.

We previously reported the synthesis of heterobi- and trimetallic complexes containing linear Cr(III)–O–Ti(IV) cores.\textsuperscript{5} The d$^1$ (omtaa)V═O complex (Scheme 3.2, omtaa: 7,16-dihydro-6,8,11,12,15,17,20,21-octamethyldibenzo[b,i][1,4,8,11]-tetraazacyclotetradecine) is a structural analogue of d$^0$ (tmtaa)Ti═O that has similar
reactivity. The V(IV) center introduces an additional unpaired electron into the resulting heterometallic systems. The magnetic orbital of this unpaired spin is strictly orthogonal to the occupied orbitals on Cr(III), as suggested by Kahn (Scheme 3.1). Such an orientation of orbitals is known to result in ferromagnetic coupling of paramagnetic metal centers and is discussed in depth elsewhere. The singly occupied d_{xy} orbitals of V(IV) and Cr(III) do not directly interact due to the absence of a symmetrically available orbital in the oxido bridge.

**Scheme 3.1** Simplified molecular geometry of V^{IV}–O–Cr^{III} in C_{4v} symmetry. The d^{1} vanadium(IV) b_{2}(d_{xy}) and d^{3} chromium(III) e(d_{xz}, d_{yz}) orbitals involved in magnetic coupling for linear V^{IV}–O–Cr^{III} are orthogonal (only one Cr magnetic orbital is shown for clarity), which results in a dominant ferromagnetic (FM) exchange interaction through a π-superexchange pathway.25,31

**3.3 Result and discussion**

Synthesis of bimetallic V=O→Cr and trimetallic [V=O→Cr←O=V]^{+} are achieved in similar reactions to those previously described, with careful control of vanadium and chromium stoichiometry (Scheme 3.2). When Cr(Por)Cl and (omtaa)V=O are combined in a 1:2 ratio, the trimetallic species 2 is isolated with a yield of 62%. In order
to synthesize bimetallic $V═O→Cr$, the electron withdrawing Cr(TFMP)Cl (TFMP: tetrakis((4-trifluoromethyl)phenyl)porphyrin) was utilized. Mixing this more reactive precursor with (omtaa)$V═O$ in a 1:1 ratio allows bimetallic 1 to be separated with a yield of 22%. As proposed in our earlier study,$^5$ the titanium containing bimetallic (tmtaa)Ti═O→Cr(Por)Cl can undergo a further exchange reaction to replace its axial chlorido ligand. Thus, the unsymmetrical trimetallic [Ti═O→Cr←O═V]$^+$ complex 3 can be prepared in 39% yield via a sequential one-pot reaction where one equivalent of (omtaa)$V═O$ is added to Ti═O→Cr prepared in situ. Attempts to synthesize 3 via a one-step, one-pot synthesis using a 1:1:1 ratio of (omtaa)$V═O$, (tmtaa)Ti═O and Cr(Por)Cl were not successful, yielding a mixture of symmetric trimetallic species.

Crystals suitable for XRD study of 1-3 were obtained by slow vapor diffusion of pentane into a dichloromethane solution. Representative molecular structures of the bi/trimetallic species are shown in Figure 3.1. Selected structural parameters and XRD experimental details are listed in Table 3.1 and Table 3.S1. As can be seen in Figure 3.1, the crystal structure of 1 indicates that the Cr(III) porphyrin and (omtaa)$V═O$ are connected by a $V═O→Cr$ interaction. The omtaa ligand undergoes a complete saddle inversion when compared to the structure of vanadium monomer (Figure 3.S5) and the $V−O−Cr$ bond angle is nearly linear with an angle of 179.10(15)$^\circ$. 
Scheme 3.2 Synthesis of V═O→Cr bimetallic complex 1 and [V═O→Cr←O═M]+ trimetallic complexes 2 (M = V) and 3 (M = Ti). (i) 1:1 ratio of (omtaa)V═O and Cr(Por)Cl in acetonitrile:toluene (1:1); (ii) 1:2:1.1 ratio of (omtaa)V═O, Cr(Por)Cl and NaSbF₆ in acetonitrile:toluene (1:1); (iii) a sequential one pot reaction: a) 1:1 ratio of (tmtaa)Ti═O and Cr(Por)Cl in acetonitrile:toluene (1:1) followed by b) an additional 1:1.1 equivalents of (omtaa)V═O and NaSbF₆.
Table 3.1 Selected bond lengths and angles for 1-3.

<table>
<thead>
<tr>
<th>Summary</th>
<th>(omtta)(\text{V═O})</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{V−O distance (Å)})</td>
<td>1.6120(8)</td>
<td>1.640(2)</td>
<td>1.649(4)</td>
<td>1.644(4)</td>
</tr>
<tr>
<td>(\text{Cr−N avg. distance (Å)})</td>
<td>n/a</td>
<td>2.025(3)</td>
<td>2.026(5)</td>
<td>2.023(4)</td>
</tr>
<tr>
<td>(\text{V−N avg. distance (Å)})</td>
<td>2.0280(9)</td>
<td>1.996(3)</td>
<td>1.997(5)</td>
<td>2.003(5)</td>
</tr>
<tr>
<td>(\text{Cr−O distance (Å)})</td>
<td>n/a</td>
<td>1.964(2)</td>
<td>1.943(4)</td>
<td>1.929(4)(^a)</td>
</tr>
<tr>
<td>(\text{V−O−Cr angle (°)})</td>
<td>n/a</td>
<td>179.10(15)</td>
<td>177.5(3)</td>
<td>177.3(2)</td>
</tr>
<tr>
<td>(\text{O−V−N avg. angle (°)})</td>
<td>108.82(4)</td>
<td>108.18(11)</td>
<td>107.94(2)</td>
<td>107.96(19)</td>
</tr>
<tr>
<td>(\text{O−Cr−N avg. angle (°)})</td>
<td>n/a</td>
<td>88.47(10)</td>
<td>89.98(18)</td>
<td>90.00(16)</td>
</tr>
</tbody>
</table>

\(^a\) \text{Cr−O−V linkage}; \(^b\) \text{Cr−O−Ti linkage}

These structural details are consistent with previous oxido-bridged bimetallic structures supported by tmtaa and porphyrin ligands.\(^2\)\(^,\)\(^5\) When comparing bimetallic 1 with (omtta)\(\text{V═O}\), the \(\text{V═O}\) bond length increases by about 0.03 Å (1.612 Å to 1.640 Å) and the \(\text{V−N}\) length is shortened by about 0.03 Å (2.028 Å to 1.996 Å). A \(\text{Cr−O}\) distance of 1.964 Å is observed, which is shorter than that of some weakly bonded O-donor Lewis bases\(^3\)\(^2\)\(^,\)\(^3\)\(^2\) but significantly longer than other unsupported oxido bridged complexes.\(^2\)\(^,\)\(^5\)\(^,\)\(^1\)\(^5\) This explains our observation that bimetallic 1 can dissociate in solution. The \(\text{Cr−Cl}\) length of 2.3405 Å in 1 is longer than that in \(\text{Cr(TPP)Cl•H}_2\text{O}\) (2.242 Å)\(^3\)\(^3\) but shorter than that in bimetallic \(\text{Ti═O→Cr−Cl}\) (2.3577 Å).\(^5\)

We conclude that the bond strength of the oxido linkage in Cr(III) porphyrins falls in the order of (tmtaa)\(\text{Ti═O}\) > (omtta)\(\text{V═O}\) > \(\text{H}_2\text{O}\), with \(\text{Cr−O}\) distances of 1.941 Å,\(^5\) 1.964 Å, and 2.239 Å\(^3\)\(^3\) respectively. Such axial structural trans influences have been
reviewed in detail elsewhere.\textsuperscript{34} The molecular structure of trimetallic 2 is depicted in Figure 3.S3 where two (omtaa)V═O groups connect to a slightly deformed Cr(III) porphyrin in a staggered geometry. A similar geometry is observed for the unsymmetric trimetallic [Ti═O→Cr←O═V]\textsuperscript{3+} (Figure 3.2), where (tmtaa)Ti═O and (omtaa)V═O are axially connected to the Cr(III) porphyrin. The Cr−O bond is shorter in the Cr−O−Ti linkage (1.929 Å) than that in the Cr−O−V linkage (1.954(4) Å). Due to the different bonding strengths of the \textit{trans} ligands, the bond length of Cr−O in heterometallic 1-3 is: 2 (1.943 Å) < 3 (1.954 Å) < 1 (1.964 Å).

\textbf{Figure 3.1} X-ray crystal structures of 1 and 3. Thermal ellipsoids are drawn at 50\% probability. Hydrogen atoms, counter ions and solvent molecules are omitted for clarity.

The temperature dependence of the magnetic susceptibility (χmol) of compounds 1-3 were measured in the temperature range 2-300 K under a constant magnetic field of 0.7 T. In Figure 3.2A, the value of χparaT for 1-3 is shown as a function of temperature T. For 1-3, χparaT increases monotonically from 300 K to a maximum value at \( \sim 40 \) K. This is typical for ferromagnetically coupled systems. The value of χparaT then
decreases as the temperature drops to 2.00 K, which can be attributed to weak intermolecular interactions and zero-field-splitting. The field-dependent magnetic behavior data measured at 2 K (Figure 3.2B) shows that the ground state is $S = 2$ for 1 and 3, while $S = 5/2$ for 2. In order to investigate the exchange coupling between Cr(III) and V(IV), we applied a simple isotropic spin Hamiltonian (equation 1), to fit the data. The final expression$^{35}$ (equation 2) is derived from the Van Vleck$^{25}$ equation where $N$ is Avogadro's number, $k_B$ is the Boltzmann constant, $T$ is the temperature, $\beta$ is the Bohr magneton, $g$ is the electron g-factor, $\theta$ is the Weiss constant, and $J$ corresponds to the net magnetic interaction between chromium and vanadium. Effects of zero-field-splitting, spin-orbital coupling, intermolecular interactions and experimental error are reflected in the small differences of the fit value for $g$.

Figure 3.2 (A), Molar magnetic susceptibility ($\chi_{\text{para}}$) plotted as $\chi_{\text{para}} \cdot T$ vs. $T$ for 1-3. Black lines represent the fit. (B) Variable field dependence of 1-3 at 2 K. (C), Exchange coupling $J$ versus Cr–O bond distance for 1-3.

$$\hat{H}_{\text{VG}} = -2J\hat{S}_v \hat{S}_\alpha, \quad \hat{S}_v = \frac{1}{2}, \quad \hat{S}_\alpha = \frac{3}{2}$$ (1)
\[
\chi_T = \frac{N g^2 \beta^2 T}{3 k_b (T - \theta)} \left( \frac{6 + 30 e^{\frac{A}{k_b T}}}{3 + 5 e^{\frac{A}{k_b T}}} \right) \tag{2}
\]

\[
\hat{H}_{\text{VGO}} = -2J (\hat{S}_v \hat{S}_\text{Cr} + \hat{S}_v \hat{S}_\text{Cr}) \quad \hat{S}_v = \frac{1}{2}, \quad \hat{S}_\text{Cr} = \frac{3}{2} \tag{3}
\]

\[
\chi_T = \frac{N g^2 \beta^2 T}{2 k_b (T - \theta)} \left( \frac{1 + 10 e^{\frac{A/2}{k_b T}} + 10 e^{\frac{A/3}{k_b T}} + 35 e^{\frac{A/4}{k_b T}}}{2 + 4 e^{\frac{A/2}{k_b T}} + 4 e^{\frac{A/3}{k_b T}} + 6 e^{\frac{A/4}{k_b T}}} \right) \tag{4}
\]

\[
J = A \times e^{\beta} \tag{5}
\]

Using this equation for 1, the values \(J = +42.5 \text{ cm}^{-1}, \theta = -0.21 \text{K}, g = 1.97\) with \(R^2 = 0.9892\) were computed. A similar result was obtained for trimetallic \([\text{Ti}═\text{O}→\text{Cr}←\text{O}═\text{V}]^+ 3\), where \(J = +44.9 \text{ cm}^{-1}, \theta = -0.26 \text{ K}, g = 1.95\) and \(R^2 = 0.9947\).

Trimetallic \([\text{V}═\text{O}→\text{Cr}←\text{O}═\text{V}]^+ 2\) was studied by a similar approach, but the presence of the second vanadium (IV) necessitated the use of a different isotropic symmetric spin Hamiltonian (equation 3). We omitted any contribution from a \(d^1-d^1\) intramolecular interaction when computing our results since the distance between the vanadium centers in 2 is quite long (7.2 Å). A simplified expression (equation 4), derived from previous reports,\(^3^6\) was applied to fit the experimental data. Using this equation for 2, \(J = +50.7 \text{ cm}^{-1}, \theta = -0.20 \text{ K}, g = 1.90\) and \(R^2 = 0.9950\) is calculated. These values for \(J\) in 1-3 are in good agreement with both the sign and magnitude of \(J\) in previous computational reports for such a \(d^1-d^3\) linkage.\(^2^9,^3^0\)
Table 3.2 Molar absorptivity of 1-3 in dichloromethane at 298 K and solid state ATR-FT-IR.

<table>
<thead>
<tr>
<th></th>
<th>UV, λ_max, nm (log ε)</th>
<th>ν_{V=O} cm^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>[a]</td>
<td>316(4.10), 377(4.44), 420 (3.90)</td>
<td>972</td>
</tr>
<tr>
<td>1</td>
<td>321(4.58), 377(4.73), 393(4.69), 446(5.20), 519(3.60), 562(3.97), 599(3.84)</td>
<td>933</td>
</tr>
<tr>
<td>2</td>
<td>329(4.67), 386(4.74), 408(4.82), 464(4.53), 535(3.75), 576(3.85), 613(3.92), 636(3.80)</td>
<td>912</td>
</tr>
<tr>
<td>3</td>
<td>344(4.76), 399(4.82), 423(4.59), 455(4.71), 526(3.76), 574(3.89), 615(3.96), 635(3.86)</td>
<td>928</td>
</tr>
</tbody>
</table>

[a] (omtaa)V═O

The distance dependence of the observed exchange coupling was fit to equation 5, with r being the Cr−O distance.\(^{37}\) It has been reported that J is correlated with the longer metal oxide bond length in asymmetric μ-oxido complexes.\(^{38}\) We therefore only considered the distance dependence caused by changes in the Cr−O bond. The value of A = 9.221×10^8 and β = -8.607 Å^{-1} is obtained by fitting the experimental data to equation 5 (Figure 3.2C). A linear fit is provided in the SI for comparison (Figure 3.59). We find that our result is consistent with the similar empirical exponential expression computed by Weihe and Güdel for oxido bridged binuclear systems. Using the metric parameters for 1-3, their model predicts that A = 2.739×10^8 and β = -7.909 Å^{-1}.\(^{39}\) The close match between our experimental result and the theoretical prediction lends support to both our experimental interpretation and their computational model. However, due to the small variations in Cr−O bond length, this is only an initial treatment for experimentally understanding magnetic coupling in such complexes. Additional compounds that have
significantly different bond lengths and/or angles will be necessary to fully model such geometric control of exchange coupling. Since the main structural differences between compounds 1-3 are in the axial ligands, we conclude that the axial ligands influence exchange coupling directly by influencing the strength of the Cr–O bond. This conclusion is consistent with the observed differences in ν_{V=O} across this series, where the largest red-shift from the mononuclear (omtta)V═O (ν_{V=O} = 972 cm⁻¹), and therefore the strongest Cr–O bond, is found for 2 (ν_{V=O} = 912 cm⁻¹, Δ = 60 cm⁻¹). The smallest shift is found for 1 (ν_{V=O} = 933 cm⁻¹, Δ = 39 cm⁻¹), which has the longest Cr–O bond as determined by crystallography (See Table 3.2)

Ferromagnetic coupling in the ground state of 2 (S =5/2) is further confirmed by variable temperature EPR (Figure 3.3). As seen in Figure 3.3, signals observed at 298 K at g = 15.7 and g = 3.60 disappear when the sample is cooled to 77 K. This is attributed to the differences in Boltzmann populations of the magnetic states, which we calculate utilizing spin ladder energies obtained using the J value determined by magnetometry. The ground state E(5/2,1) is populated at 69.6% at 298 K, but rises to 96.7% at 77 K. The signals at g = 15.7 and 3.60 are assigned to the EPR response from the nearest excited spin state E(3/2, 0) is calculated to be 16.8% populated at 298 K and 2.9% at 77 K. Simulation of these states was performed using the Easyspin package, resulting in g = 1.97, |D| = 0.041 cm⁻¹, |E| = 0.019 cm⁻¹ for E(5/2, 1) and g = 1.96, |D| = 0.191 cm⁻¹, |E| = 0.010 cm⁻¹ for the E(3/2, 0) state.

This work confirms the long standing prediction of ferromagnetic exchange coupling in linear oxido-bridged d¹-d³ systems. This V(IV)–O–Cr(III) d¹-d³ oxido bridged system provides the first examples of a ground state analogue for the d¹-d³ excited state
that results from MMCT of a d⁰-d⁴ species such as Ti(IV)–O–Mn(III) (Scheme 3.3).⁴¹

We propose that measuring properties such as exchange coupling in these models can provide guidance when designing species with long-lived MMCT transitions.

 Processes for light induced MMCT are depicted in Scheme 3.3. In case A, the ground state has the quintet ⁵[d⁰-d⁴hs] with a high spin d⁴ metal site (Scheme 3.3a). Other systems containing MMCT transitions, such as Cr(III)-O-Ti(IV) (d⁰-d³),⁴² Mn(II)-O-Ti(IV) (d⁰-d⁵),⁴³ can be modeled in a similar manner. In this simplified model, the initial ground state ⁵[d⁰-d⁴hs] can be excited into the corresponding ⁵[d¹-d³] MMCT excited state. Depending on the sign of the exchange coupling between the d¹ and d³ metal
centers in this state, the initially populated $^5[d^1\cdots d^3]$ can intersystem cross to form a $^3[d^1\cdots d^3]$ state of relatively lower energy. If the $d^1$ and $d^3$ sites are antiferromagnetically coupled in the excited state ($2J < 0$), the triplet $^3[d^1\cdots d^3]$ will be lower energy than the quintet $^5[d^1\cdots d^3]$ (Scheme 3.3a). As suggested by McClure and Frei, this subsequently populated spin state would create a spin forbidden barrier for back electron transfer, slowing the rate for repopulation of the ground state.$^{13}$ Known examples of such long-lived chromophores, analogous to organic and inorganic triplet excited states, have been reported.$^{44}$ It has been shown theoretically$^{30}$ and experimentally$^{45}$ that antiferromagnetic coupling values increase as the angle of the $M\cdots O\cdots M'$ linkages decrease. Based on their determination of a significantly bent $Ti^{IV}\cdots O\cdots Mn^{II}$ structure ($\sim 110^\circ$) in surface bound MMCT chromophores,$^{13,46}$ we propose that such excited states should exhibit antiferromagnetic coupling between the photoexcited $Ti^{III}\cdots d^1$ and $Mn^{III}\cdots d^4$ metal centers. This geometrically enforced antiferromagnetic coupling is the origin of a low lying $^4[d^1\cdots d^4]$ state, which ultimately slows BET to regenerate the $^6[d^0\cdots d^5]$ ground state in such chromophores.
Scheme 3.3 A) Formation of a d\(^{1}\)-d\(^{3}\) MMCT excited state from a d\(^{0}\)-d\(^{4}\) heterobimetallic chromophore; B) Intersystem crossing to energetically lower state C) Exchange coupling of this excited state can determined by d\(^{1}\)-d\(^{3}\) heterobimetallic molecules ground state analogues. In all systems, ground states are shown in red, initial excited states are shown in blue and spin-trapped states are green. Ground state analogues of the spin-trapped states are shown in orange.

A similar spin forbidden BET barrier can be imagined for systems with ferromagnetic coupling, such as the linear systems reported here. As shown in Scheme 3.3b, such a complex would require a ground state \(^{3}[d^{0}\cdot d^{4}]_{ls}\) with a low spin d\(^{4}\) metal site, such as low spin Mn\(^{III}\).\(^{47}\) This initial ground state \(^{3}[d^{0}\cdot d(ls)^{4}]\) can be excited to form its corresponding \(^{3}[d^{1}\cdot d^{3}]\) excited state. In this case, ferromagnetic coupling would be present between the excited state d\(^{1}\) and d\(^{3}\) centers (2\(J > 0\)). Therefore, the quintet \(^{5}[d^{1}\cdot d^{3}]\) state will be lower in energy when compared with a triplet \(^{3}[d^{1}\cdot d^{3}]\) state. It is known that spin multiplicity can be altered in the excited state, with MMCT inducing
magnetization changes in solid-state cyano-bridged assemblies. This new model suggests that such linear heterobimetallic complexes, with low-spin donor metal sites, can also be synthetic targets for realizing chromophores with long-lived MMCT transitions.

Experimental measurements of exchange coupling in MMCT excited states are known to be complicated. As demonstrated here, measuring exchange coupling in ground state analogues of these excited states is much more straightforward. We speculate that the sign and magnitude of excited state exchange coupling may play important role on the BET rate of MMCT excited states. The sign and magnitude of exchange coupling in charge transfer excited states is known to influence BET in organic chromophores, with ground state analogues able to predict such effects. Recently, our group reported the synthesis of $d^1-d^x (x = 5-9)$ unsupported oxido bridged complexes with various $M_1-O-M_2$ angles (156°~170°) and M-O distances (1.94~2.09 Å) which could also serve as ground state analogues of additional MMCT excited states.

The connection between the sign and magnitude of $J$ and MMCT lifetimes in such heterobimetallic compounds remains speculative, however the compounds reported here represent an important step toward providing the quantitative measurements necessary to experimentally and theoretically model the influence of excited state magnetic coupling on the lifetimes of MMCT-based chromophores.

3.4 Conclusion

In summary, we have developed approaches to synthesize the first examples of $V(IV)–O–Cr(III)$, $V(IV)–O–Cr(III)–O–Ti(IV)$ and $V(IV)–O–Cr(III)–O–V(IV)$ species. Ferromagnetic exchange coupling is observed between the metal centers in
these $d^1$-$d^3$ (1), $d^1$-$d^3$-$d^0$ (3) and $d^1$-$d^3$-$d^1$ (2) systems. The magnitude of this interaction is found to be influenced by the trans axial ligand and is consistent with an empirical distance dependent equation: $J = Ae^{\beta r}$, where $A = 9.221 \times 10^8$ and $\beta = -8.607 \text{Å}^{-1}$. To our knowledge, this is the first direct experimental evidence of ferromagnetic exchange in an unsupported oxido bridged heterometallic species and confirms that an empirical relationship which depends on angular and distance dependence can be applied to predict exchange coupling between two different paramagnetic centers. Such data is of particular importance for understanding magnetic control of MMCT excited state lifetimes in oxido-bridged heterobimetallic chromophores in both homogeneous and heterogeneous systems.

3.5 Experimental section

3.5.1 General procedures.

All reactions were performed under an atmosphere of nitrogen in an Innovative Technology glovebox or using Schlenk techniques. All chemicals were purchased from VWR International, Sigma Aldrich, Alfa Aesar or TCI America and used without further purification. All solvents were stored over 4Å molecular sieves prior to use. Dichloromethane and pentane were sparged with $N_2$ and dried over an alumina column using the method of Grubbs.$^{60}$ Toluene was dried over purple sodium benzophenone ketyl, then vacuum transferred and freeze-pump-thawed before storing in Teflon-sealed Schlenk bombs. Acetonitrile was dried over CaH$_2$ and distilled prior to use. Absorption spectra were recorded on an Olis RSM-1000 spectrometer using 1 cm Teflon-sealed quartz cuvettes. Attenuated total reflectance (ATR)mFTIR spectra were recorded with either a Bruker Vertex 80V infrared spectrometer equipped with a Platinum™ Diamond
ATR attachment or a Bruker Alpha ATR-FTIR. Magnetic susceptibilities were measured on a Quantum Design MPMS-XL7 SQUID Magnetometer. A saturation plot was measured at 2 K with the applied field being varied from 0~70000 oe. Temperature-dependent magnetic susceptibilities were performed from 2-300 K. Crystalline samples (ca. 10-30 mg) were loaded into gelcap/straw sample holders and mounted to the sample rod with Kapton tape for temperature dependence measurements. For compound 1-3, multiple measurements were performed. The fitting results (such as g-factor, θ and J) from these separate data sets are consistent. The reported error bars for J are based on several separate fitting results from different data sets. Electron paramagnetic resonance spectra were taken with samples at either at room temperature or at 77 K in a Bruker ELEXSYS E500 spectrometer operating at approximately 9.86 GHz (X-band) with a modulation amplitude of 10 G and a modulation frequency of 100 kHz. The experimental time constant was set at 81.92 ms with a 117.19 ms conversion time and a 120 s sweep time. A typical collection of 1024 data points is performed under 2 mW incident microwave power in a range from 0 to 8000 G. Recrystallized polycrystalline solid samples (1 ~ 2 mg) were loaded in Wilmad® quartz (CFQ) EPR tubes (O.D. 4 mm, L 100 mm) and sealed under N2.

The ligands studied in this report are represented by the following abbreviations: TPP, tetraphenylporphyrin; TFMP, tetrakis((4-trifluoromethyl)phenyl)porphyrin; tmtaa: 7,16-dihydro-6,8,15,17-tetramethyldibenzo[b,i][1,4,8,11]tetraazacyclocotetradecine, omtaa: 7,16-dihydro-6,8,11,12,15,17,20,21-octamethyldibenzo[b,i][1,4,8,11]tetraazacyclotetradecine. The ligands are synthesized according to the reports of
Weare and coworkers\textsuperscript{5} and Goedken and coworkers.\textsuperscript{19} Cr(III) porphyrin,\textsuperscript{5}, (tmtaa)Ti═O and (omtaa)V═O\textsuperscript{19} are synthesized as previously reported.

3.5.2 X-Ray crystallography

Crystals were mounted on MiTeGen mounts and cooled to 110 K. X-ray intensity data were measured on a Bruker-Nonius X8 Kappa APEX II system equipped with a graphite monochromator and a MoKα fine-focus sealed tube (λ = 0.71073 Å). Unit cell dimensions were determined from symmetry constrained fits of the reflections. Frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the multi-scan method (SADABS). Structures were solved using direct methods (Bruker XS) and refined using the Bruker SHELX 2013\textsuperscript{61} software package using full-matrix least-squares refinement on F. All non-hydrogen atoms were identified in the original solution, or located from the difference map from refinement results. Hydrogen atoms were placed at idealized positions and allowed to ride on the nearest non-H atom. Figures of the molecular structures were created using Olex2 Crystallographic information files for all structures are available in the ESI\textsuperscript{†} and from the Cambridge Crystallographic Data Center (www.ccdc.cam.ac.uk). CCDC reference number: 1 (1049246), 2 (1049245), 3 (1049247), (omtaa)V═O (1049244).

3.5.3 Synthesis of (omtaa)V═O→Cr(R)Cl binuclear complexes,

(omtaa)V═O→Cr(TFMP)Cl, (1). The synthesis is adopted from a previous publication.\textsuperscript{2} In the glovebox, (omtaa)V═O (50.0 mg, 0.11 mmol) and Cr(TFMP)Cl (104.4 mg 0.11 mmol) were added to 5 mL of a 1:1 acetonitrile:toluene mixture in a 50 mL Teflon-sealed Schlenk flask and heated at 80 ºC for 12 h. The solution was then
cooled slowly to room temperature and was filtered to remove side products. A fine green powder was obtained from the filtrate after removal of the solvent in vacuo. The final product, which is of X-ray quality, was obtained after recrystallization via layered diffusion of pentane (15 mL) into a dichloromethane (3 mL) solution at -25 °C. Yield after recrystallization: 43.6 mg, 28.2%. UV/Vis (CH₂Cl₂) λ_max (nm) (ε (M⁻¹cm⁻¹)): 321 (38300), 377 (53500), 393 (48500), 446 (160000), 519 (4000), 562 (9400), 599 (6900). ATR/FTIR ν_V=O (cm⁻¹): 933(s). Anal. calc'd for C₇₄H₅₄ClCrF₁₂N₈OV • 0.5CH₂Cl₂: C, 60.58; H, 3.75; N, 7.59. Found: C, 60.16; H, 3.63; N, 7.67. HRMS-ESI (M⁺) calc’d for C₇₄H₅₄ClCrF₁₂N₈OV: 1401.3068. Found 1401.3049.

3.5.4 Synthesis of [(omtaa)V=O→Cr(R)←O=V(omtaa)]⁺ trinuclear complexes, [(omtaa)V=O→Cr(TPP)←O=V(omtaa)]SbF₆, (2). The compound was synthesized and purified by following a procedure similar to that described above for 1 using two equivalents of (omtaa)V=O (50.0 mg, 0.11 mmol), one equivalent of Cr(TPP)Cl (37.6 mg 0.054 mmol) and 1.1 equivalents of NaSbF₆ (17.5 mg, 0.067 mmol). X-ray quality crystals were obtained via vapor diffusion of pentane into a solution of dichloromethane at room temperature. Yield after recrystallization: 60.9 mg, 62%. UV/Vis (CH₂Cl₂) λ_max (nm)(ε (M⁻¹cm⁻¹)): 329 (46300), 386 (55400), 408 (66000), 464 (33700), 535 (5600), 576 (7100), 613 (8300), 636 (6300). ATR/FTIR ν_V=O (cm⁻¹): 912(s). Anal. calc’d for C₉₆H₈₈CrF₆N₁₂O₂SbV₂, C, 56.77; H, 4.28; N, 8.11. Found: C, 56.10; H, 4.04; N, 8.40. HRMS-ESI (M⁺) calc’d for C₉₆H₈₈CrN₁₂O₂V₂: 1594.5432. Found 1594.5423.
3.5.5 Synthesis of [(tmtaa)Ti═O→Cr(R)←O═V(omtaa)]⁺ trinuclear complexes, [(tmtaa)Ti═O→Cr(TPP)←O═V(omtaa)]SbF₆, (3). The compound was synthesized in a sequential two-step, one-pot procedure utilizing methods similar to those described above for 1. In the glovebox, equimolar amounts of (tmtaa)Ti═O (50.0 mg, 0.12 mmol) and Cr(TPP)Cl (86.0 mg 0.12 mmol) were added to 12 mL of a 1:1 acetonitrile:toluene mixture in a 50 mL Teflon-sealed Schlenk flask and heated at 80 °C for 12 h. Following this step, one equivalent of (omtaa)V═O (57.2 mg, 0.12 mmol) and 1.1 equivalents of NaSbF₆ (35.0 mg, 0.14 mmol) were added into mixture and the reaction is stirred for an additional 12 h at 80 °C. The solution was then cooled slowly to room temperature and was filtered to remove side products. After filtration, a fine green powder was obtained after removal of the solvent in vacuo. The resulting solid was purified similarly to 1. X-ray quality crystals were obtained via vapor diffusion of pentane into a solution of dichloromethane at room temperature. Yield after recrystallization: 85.6 mg, 39.2%. Attempts to make 3 in a single step by adding all of the starting materials at once yielded a mixture of the Ti only (compound 8 in reference 5) and V only (2) heterotrimallelic compounds as identified by ESI-MS. UV/Vis (CH₂Cl₂) \( \lambda_{\text{max}} \) (nm)(ε (M⁻¹cm⁻¹)): 344 (56900), 389 (65800), 423 (38600), 455 (51000), 526 (5800), 574 (7700), 615 (9100), 635 (7300). ATR/FTIR ν_{V═O} (cm⁻¹): 928(s), ν_{Ti═O} (cm⁻¹): 911(s). Anal. calc’d for C₉₂H₆₀CrF₆N₁₂O₂SbTiV•0.5CH₂Cl₂: C, 61.16; H, 5.00; N, 9.35. Found: C, 61.22; H, 4.50; N, 9.26. HRMS-ESI (M⁺) calc’d for C₉₂H₆₀CrN₁₂O₂TiV: 1535.4845. Found 1535.4857.
3.6 Supporting information

Details of electronic absorption spectra

![Graph showing electronic absorption spectra](image)

**Figure 3.S1.** A) Molar absorptivity of the (omtaa)V═O, Cr(TPP)Cl, bimetallic 1 and trimetallic 2-3 in dichloromethane.

The electronic absorption spectra of 1-3 are depicted in Figure 3.S1 and summarized in Table 3.S1. As can be seen in Figure 3.S1, the change of the absorption spectrum of 1 is not significant when compared to its precursors. The (omtaa)V═O based absorption has a small red shift from 316 nm to 321 nm and the porphyrin based Soret band and Q bands remain similar to the Cr(III) porphyrin precursor. The small differences in electronic absorption spectra is in contrast to previous examples of bimetallic Ti═O→Cr. We believe the (omtaa)V═O in this bimetallic species can dissociate in solution at room temperature since the V═O→Cr is relative weakly bonded. Contrary to the small change in bimetallic species, the
Soret band in trimetallic species is red shifted to 464 nm and the intensity dramatically decreases. The (omtaa)V═O based absorption at 420 nm is blue shifted to 408 nm and gains intensity. This intensity borrowing suggests a configuration interaction between these two chromophores. Detailed study of this unusual configuration interaction is still in progress. By comparing the electronic absorption spectrum of 2-3 with the precursor molecules and bimetallic species 1, we conclude the trimetallic species remains stable in solution otherwise these significant differences in electronic absorption spectrum would not be observed.

Solid state ATR-FTIR spectra of 1-3 are depicted in Figure 3.S6-8 and summarized Table 3.S1. The V═O stretch is red shifted by 40~60 cm⁻¹ when coordinated to chromium, which is in agreement with Goedken and coworkers. The lower energy νV═O in 2 indicates that a stronger bonding interaction occurs in V═O→Cr than in the V═O→BPh₃ observed by Goedken. As shown in Table 3.S1, the bimetallic species 1 has νV═O at 933 cm⁻¹ while trimetallic species 2 has νV═O frequency at 912 cm⁻¹. This shows a stronger interaction in the trimetallic species than the bimetallic species which is presumably due to different electronic properties of axial ligands as proposed in our previous study. In trimetallic species, the (omtaa)V═O is believed to stabilize a second (omtaa)V═O which is trans to itself via a push-pull mechanism. This observation is also consistent with the suggested instability of 1 in solution as observed using EAS.
X-ray Crystallography

**Figure 3.S2.** X-ray crystal structure of 1. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms and solvent molecules are omitted for clarity.

A dark black block-like specimen of C$_{80}$H$_{66}$Cl$_{13}$CrF$_{12}$N$_8$OV, approximate dimensions 0.568 mm × 0.391 mm × 0.274 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

A total of 1097 frames were collected. The total exposure time was 21.53 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a orthorhombic unit cell yielded a total of 102867 reflections to a maximum θ angle of 26.373° (0.80 Å resolution), of which 18323 were independent (average redundancy 5.61, completeness = 100.0 %, Rint = 4.28%, Rsig = 3.87%) and 13275
(72.45%) were greater than 2σ(F²). The final cell constants of \( a = 13.1820(5) \) Å, \( b = 13.6961(6) \) Å, \( c = 27.0875(11) \) Å, volume = 4485.3(3) Å³, are based upon the refinement of the XYZ-centroids of 9681 reflections above 20 σ(I) with 4.674° < 20 < 52.904°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.8347.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P-1, with \( Z = 2 \) for the formula unit, \( \text{C}_{80}\text{H}_{66}\text{Cl}_{13}\text{CrF}_{12}\text{N}_{8}\text{OV} \). The final anisotropic full-matrix least-squares refinement on \( F^2 \) with 1092 variables converged at \( R_1 = 5.56 \% \), for the observed data and \( wR_2 = 16.55 \% \) for all data. The goodness-of-fit was 1.044. The largest peak in the final difference electron density synthesis was 0.958 e/Å³ and the largest hole was -1.005 e/Å³ with an RMS deviation of 0.094 e/Å³. On the basis of the final model, the calculated density was 1.442 g/cm³ and \( F(000) \), 1972.0 e⁻.
Figure 3.S3. X-ray crystal structure of 2. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms, SbF$_6$ anion and solvent molecules are omitted for clarity.

A metallic dark black block-like specimen of C$_{100}$H$_{96}$Cl$_8$CrF$_6$N$_{12}$O$_2$Sb$_2$, approximate dimensions 0.716 mm × 0.598 mm × 0.296 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

A total of 465 frames were collected. The total exposure time was 21.76 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 108776 reflections to a maximum θ angle of 25.680° (0.82 Å resolution), of which 18697 were independent (average redundancy 5.82, completeness = 99.8 %, Rint = 8.37%, Rsig = 4.66%) and 14133
(75.59%) were greater than 2σ(F²). The final cell constants of \(a = 21.3129(7) \text{ Å}, b = 22.2548(7) \text{ Å}, c = 24.0941(9) \text{ Å}, \text{ volume} = 9869.3(6) \text{ Å}^3\), are based upon the refinement of the XYZ-centroids of 9996 reflections above 20 \(σ(I)\) with 4.716° < 2θ < 51.510°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.7444.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group \(P2_1/c\), with \(Z = 4\) for the formula unit, \(\text{C}_{100}\text{H}_{96}\text{Cl}_{8}\text{CrF}_{6}\text{N}_{12}\text{O}_{2}\text{SbV}_{2}\). The final anisotropic full-matrix least-squares refinement on \(F^2\) with 1251 variables converged at \(R_1 = 8.26\%\), for the observed data and \(wR_2 = 22.82\%\) for all data. The goodness-of-fit was 1.081. The largest peak in the final difference electron density synthesis was 1.193 e/Å³ and the largest hole was -1.599 e/Å³ with an RMS deviation of 0.067 e/Å³. On the basis of the final model, the calculated density was 1.461 g/cm³ and \(F(000) = 4427.9\text{ e}^\cdot\).
Figure 3.S4. X-ray crystal structure of 3. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms, SbF$_6$ anion and solvent molecules are omitted for clarity.

A metallic dark black plate-like specimen of C$_92$H$_80$CrF$_6$N$_{12}$O$_2$SbTiV, approximate dimensions 0.506 mm × 0.465 mm × 0.120 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 2337 frames were collected. The total exposure time was 42.80 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a orthorhombic unit cell yielded a total of 203167 reflections to a maximum θ angle of 25.027° (0.84 Å resolution), of which 16810 were independent (average redundancy 12.28, completeness = 100.0 %, Rint = 4.09%, Rsig = 2.29%) and 12900 (76.74%) were greater than 2σ(F$^2$). The final cell constants of a = 18.4365(8) Å, b =
22.6229(10) Å, c = 24.1293(10) Å, volume = 9523.6(5) Å³, are based upon the refinement of the XYZ-centroids of 9054 reflections above 20 σ(I) with 4.876° < 2θ < 50.568°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.8833.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P2₁/C, with Z = 4 for the formula unit, C₉₂H₈₀CrF₆N₁₂O₂SbTiV. The final anisotropic full-matrix least-squares refinement on F² with 1109 variables converged at R₁ = 7.74 %, for the observed data and wR₂ = 21.22 % for all data. The goodness-of-fit was 1.150. The largest peak in the final difference electron density synthesis was 0.820 e⁻/Å³ and the largest hole was -1.006 e⁻/Å³ with an RMS deviation of 0.090 e⁻/Å³. On the basis of the final model, the calculated density was 1.474 g/cm³ and F(000), 3624.0 e⁻.

**Figure 3.S5.** X-ray crystal structure of (omtaa)V═O. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms and solvent molecules are omitted for clarity.
A metallic dark black plate-like specimen of C$_{27}$H$_{32}$Cl$_2$N$_4$OV, approximate dimensions 0.575 mm × 0.320 mm × 0.212 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

A total of 2547 frames were collected. The total exposure time was 18.43 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a orthorhombic unit cell yielded a total of 43863 reflections to a maximum θ angle of 32.577° (0.66 Å resolution), of which 9191 were independent (average redundancy 4.77, completeness = 100.0 %, Rint = 1.47%, Rsig = 2.05%) and 8578 (93.33%) were greater than 2σ(F$^2$). The final cell constants of a = 8.5779(7) Å, b = 12.0788(10) Å, c = 12.8219(11) Å, volume = 1263.52(18) Å$^3$, are based upon the refinement of the XYZ-centroids of 9734 reflections above 20 σ(I) with 4.908° < 2θ < 78.398°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.8669.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P-1, with Z = 4 for the formula unit, C$_{27}$H$_{32}$Cl$_2$N$_4$OV. The final anisotropic full-matrix least-squares refinement on F$^2$ with 343 variables converged at R$_1$ = 3.30 %, for the observed data and wR$_2$ = 9.81 % for all data. The goodness-of-fit was 1.057. The largest peak in the final difference electron density synthesis was 0.583 e-/Å$^3$ and the largest hole was -0.813 e-/Å$^3$ with an RMS deviation of 0.072 e-/Å$^3$. On the basis of the final model, the calculated density was 1.447 g/cm$^3$ and F(000), 574.0 e$^-$. 

Electronic absorption and solid state ATR-FTIR spectra of 1-3

Figure 3.S6. Molar absorptivity (in dichloromethane) and solid state ATR-FTIR spectra of 1.
Figure 3.S7. Molar absorptivity (in dichloromethane) and solid state ATR-FTIR spectra of 2.
Figure 3.S8. Molar absorptivity (in dichloromethane) and solid state ATR-FTIR spectra of 3.
HRMS-ESI results of 1-3 including simulated patterns for [M]$^+$ and [M+H]$^+$.  

**Figure 3.S9.** HRMS-ESI and simulated patterns of [M]$^+$, [M+H]$^+$ for 1.

**Figure 3.S10.** HRMS-ESI and simulated patterns of [M]$^+$, [M+H]$^+$ for 2.
Figure 3.S11. HRMS-ESI and simulated patterns of [M]$^+$, [M+H]$^+$ for 3
**Figure 3.S12.** Exchange coupling $J$ versus Cr–O bond distance for 1-3. Linear fit is performed as comparison to exponential fit which illustrates that $a = 834.5$ and $b = -403.6$ Å for equation of $J = a \times r + b$.

\[ J = A \times e^{br} \]
\[ A = 9.221 \times 10^8 \]
\[ \beta = -8.607 \]

**Figure 3.S13.** Overlay of ATR-FTIR spectra of (omtaa)V=O and 1-3.
### Table 3.S1. Crystal data and structure refinement details for 1-3

<table>
<thead>
<tr>
<th>Identification</th>
<th>(omtaa)V═O</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ccde number</td>
<td>1049244</td>
<td>1049246</td>
<td>1049245</td>
<td>1049247</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C_{27}H_{32}Cl_{2}N_{4}</td>
<td>C_{36}H_{48}Cl_{11}CrF_{12}N_{8}</td>
<td>C_{100}H_{96}Cl_{8}CrF_{6}N_{12}O_{2}S</td>
<td>C_{29}H_{30}CrF_{6}N_{12}O_{2}Sb</td>
</tr>
<tr>
<td>Formula weight</td>
<td>550.4</td>
<td>1947.19</td>
<td>2171.11</td>
<td>1772.27</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>110</td>
<td>110.1</td>
<td>100.07</td>
<td>110.1</td>
</tr>
<tr>
<td>Crystal system</td>
<td>triclinic</td>
<td>triclinic</td>
<td>monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
<td>P-1</td>
<td>P2_{1}/c</td>
<td>P2_{1}/c</td>
</tr>
<tr>
<td>a/Å</td>
<td>8.5779(7)</td>
<td>13.1820(10)</td>
<td>19.3129(7)</td>
<td>18.4365(8)</td>
</tr>
<tr>
<td>b/Å</td>
<td>12.0788(10)</td>
<td>13.6961(6)</td>
<td>22.2548(7)</td>
<td>22.6229(10)</td>
</tr>
<tr>
<td>c/Å</td>
<td>12.8219(11)</td>
<td>27.0875(11)</td>
<td>24.0941(9)</td>
<td>24.1293(10)</td>
</tr>
<tr>
<td>α/°</td>
<td>79.362(4)</td>
<td>101.953(2)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β/°</td>
<td>78.253(4)</td>
<td>95.065(2)</td>
<td>107.631(2)</td>
<td>108.861(2)</td>
</tr>
<tr>
<td>γ/°</td>
<td>79.424(4)</td>
<td>108.123(2)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Volume/Å³</td>
<td>1263.52(18)</td>
<td>4485.3(3)</td>
<td>9869.3(6)</td>
<td>9523.6(7)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>2</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>ρ_{calclg}/cm³</td>
<td>1.447</td>
<td>1.442</td>
<td>1.461</td>
<td>1.236</td>
</tr>
<tr>
<td>μ/mm⁻¹</td>
<td>0.633</td>
<td>0.685</td>
<td>0.845</td>
<td>0.629</td>
</tr>
<tr>
<td>F(000)</td>
<td>574</td>
<td>1972</td>
<td>4428</td>
<td>3624</td>
</tr>
<tr>
<td>Crystal size/mm³</td>
<td>0.575 × 0.32</td>
<td>0.568 × 0.391 × 0.274</td>
<td>0.716 × 0.598 × 0.294</td>
<td>0.506 × 0.465 × 0.12</td>
</tr>
<tr>
<td>Radiation</td>
<td>MoKα (λ = 0.71073)</td>
<td>MoKα (λ = 0.71073)</td>
<td>MoKα (λ = 0.71073)</td>
<td>MoKα (λ = 0.71073)</td>
</tr>
<tr>
<td>2Θ range for data collection/°</td>
<td>3.47 to 65.154</td>
<td>1.558 to 52.746</td>
<td>2.212 to 51.36</td>
<td>2.948 to 50.054</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-12 ≤ h ≤ 12,</td>
<td>-16 ≤ h ≤ 16, -17 ≤ k ≤ 17, -33 ≤ l ≤ 33</td>
<td>-18 ≤ h ≤ 23, -27 ≤ k ≤ 27, -29 ≤ l ≤ 29</td>
<td>-21 ≤ h ≤ 21, -26 ≤ k ≤ 26, -28 ≤ l ≤ 28</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>43863</td>
<td>102867</td>
<td>108776</td>
<td>203167</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>9191 [R_{int} = 0.0205, R_{sigma} = 0.0147]</td>
<td>18323 [R_{int} = 0.0428, R_{sigma} = 0.0387]</td>
<td>18697 [R_{int} = 0.0837, R_{sigma} = 0.0466]</td>
<td>16810 [R_{int} = 0.0409, R_{sigma} = 0.0229]</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>9191/0/343</td>
<td>18323/0/1092</td>
<td>18697/1/1251</td>
<td>16810/11/1109</td>
</tr>
<tr>
<td>Goodness of-fit on F²</td>
<td>1.057</td>
<td>1.044</td>
<td>1.081</td>
<td>1.15</td>
</tr>
<tr>
<td>Final R indexes [I&gt;=2σ (I)]</td>
<td>R₁ = 0.0330, wR₂ = 0.0959</td>
<td>R₁ = 0.0556, wR₂ = 0.1421</td>
<td>R₁ = 0.0826, wR₂ = 0.1926</td>
<td>R₁ = 0.0774, wR₂ = 0.1933</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>R₁ = 0.0355, wR₂ = 0.0981</td>
<td>R₁ = 0.0840, wR₂ = 0.1655</td>
<td>R₁ = 0.1166, wR₂ = 0.2282</td>
<td>R₁ = 0.1012, wR₂ = 0.2122</td>
</tr>
<tr>
<td>Largest diff. peak/hole / e Å⁻³</td>
<td>0.58/-0.81</td>
<td>0.96/-1.00</td>
<td>1.19/-1.60</td>
<td>0.82/-1.01</td>
</tr>
</tbody>
</table>
3.7 Acknowledgements

This work was supported by generous startup funding from North Carolina State University. We acknowledge John C. Ledford, Dr. Daniel Stasiw and Prof. David A. Shultz for assistance in collecting SQUID data. Mass spectra were obtained at the NCSU Department of Chemistry Mass Spectrometry Facility. The EPR instrumentation used in this work was supported by NSF CHE-0840501.

3.8 References


(64) Buchler, J.; Kokisch, W.; Smith, P. In *Novel Aspects Structure and Bonding*; Springer Berlin Heidelberg: 1978; Vol. 34, p 79.
CHAPTER 4

Tuning Metal-Metal Interactions with a Simple Molecular Twist

This work was submitted to Chem. Sci.


Huang, T performed all general characterization, magnetization work and worked with Sommer, R. D. to conduct X-ray diffraction experiment. The synthesis was performed by Huang, T and Wu, X.

Department of Chemistry, North Carolina State University;

Raleigh, NC, 27695-8204
4.1 Abstract
A twisted heterobimetallic oxido-bridged complex V(IV)−O−Mn(III) (2) was synthesized and structurally characterized. Temperature-dependent magnetic susceptibility and variable-field magnetization indicate a ferromagnetic coupling between d¹ V(IV) and d⁴ Mn(III) with a weak $J$ of +3 cm⁻¹ ($H = -2J S_V S_M$). This exchange coupling constant is an order of magnitude weaker than in previously reported analogues with similar structures: V(IV)−O−Cr(III) (1) and V(IV)−O−Mn(II) (3) in which $J$ = +43 cm⁻¹ and +37 cm⁻¹, respectively. This result significantly deviates from previous empirical models that describe magnetic interactions in mononuclear-bridged bimetallic molecules. We ascribe this result to the impact of a molecular twist, which results in poor $d_\pi-p_\pi$ orbital overlap through the oxido linkage. The torsion angle for this twist was determined to be 2.6°, 39.3°, and 9.5° for 1-3, respectively. The large torsion angle in 2 diminishes electronic coupling between the paramagnetic centers, suggesting that molecular twisting, and the resulting changes in $d_\pi-p_\pi$ overlap, can be used to modify electronic or magnetic coupling in simple mononuclear-bridged species.

4.2 Introduction
Materials with controllable magnetic behaviors are vital as components in modern technologies. As such, exploration of molecules with tunable molecular magnetic properties continues to be a fertile area of study. Efforts which utilize molecules for spin transport,¹⁻⁵ molecular switches⁶⁻⁹ and single molecule magnets¹⁰⁻¹² show promise for achieving molecular scale electronics, magnetic data storage and quantum computing.¹³⁻¹⁵ The search for molecules that exhibit interesting magnetic behaviors has evoked considerable attention on controllable synthetic approaches for functionalized and magnetically-active molecules.¹⁶
Transition metal oxides are known to be promising magnetic materials.\textsuperscript{17-22} However, their properties are difficult to tune on a molecular level. In contrast, homometallic and heterometallic complexes have been extensively employed as structural models for understanding and controlling the quantum chemical basis for molecular magnetism.\textsuperscript{23} This includes determining the sign and magnitude of exchange coupling within polynuclear centers,\textsuperscript{24-28} theoretical analysis of the origins of such interactions\textsuperscript{28-31} and the establishment of magneto-structural relationships.\textsuperscript{32}

Heterometallic complexes with unsupported oxido-bridges have been synthetically challenging targets.\textsuperscript{33,34} The development of additional synthetic strategies\textsuperscript{35} and improvements in their structural characterization\textsuperscript{36} have significantly expanded the availability of such compounds, particularly for hetero bi/trimetallic species containing first row transition metals. This has provided an opportunity to model and explore the magneto-structural properties of such simple bridges. For example, a long-standing theoretical prediction for a dominant ferromagnetic pathway in linear oxido heterobimetallic species was recently confirmed,\textsuperscript{37} and a correlation proposed that links the ground-state magnetic properties in such complexes to the electronic coupling in metal-to-metal charge transfer excited states.\textsuperscript{37,38}

In contrast to the many well-studied bridged systems with geometries that are relatively rigid,\textsuperscript{26} an unsupported bridge has the flexibility to allow rotation or twisting.\textsuperscript{39-43} Altering geometries via bridge rotation in coupled paramagnetic systems has been found to control spin-spin interactions and can influence physical properties such as electronic coupling, electron conductance and charge transfer.\textsuperscript{44-46} To the best of our knowledge, demonstration of magneto-structural relationships which result from
geometric twisting in simple mononuclear-bridged metallic compounds remains unknown. Such twisting would result in variation of the overlap between dπ-pπ or dπ-dπ orbitals, which should modify the magnetic and electronic properties of these molecules.

Here we report the synthesis and structure of a twisted V(IV)-O-Mn(III) heterobimetallic oxido complex: (omtaa)V═O→Mn(TMP)SbF₆ (2), (omtaa = 7,16-dihydro-6,8,11,12,15,17,20,21-octamethyldibenzo[b,i][1,4,8,11]tetraazacyclotetradecine, TMP = tetrakis((4-methoxyl)phenyl)por-phyrin). We compare the magneto-structural properties of 2 with two similar untwisted systems: (omtaa)V═O→Cr(TFMP)Cl (1) and (tmtaa)V═O→Mn(Py₅Me₂)(OTf) (3). This comparison illustrates, for the first time, that exchange coupling can be controlled using by varying the torsion angle along these simple bridges. (Figure 4.1).

Figure 4.1 Comparison of the magneto-structural properties of 1-3. $J_{\text{calc}}$ is computed using previously reported empirical parameters with corrections from an angular overlap model.³⁰,³²,⁴⁷
4.3 Result and discussion

The synthesis of 2 was achieved through the reaction of one equivalent of (omtaa)\(V=O\) with one equivalent of Mn(TMP)SbF\(_6\) in dichloromethane at room temperature under \(N_2\) protection (Scheme 4.1). Suitable crystals for single X-ray crystallographic analysis can be obtained using vapor diffusion in a pentane/dichloromethane system at -20 °C. The structure of 2 is depicted in Figure 4.S1, which shows a Mn–O length of 2.080 Å and \(V=O\) length of 1.654 Å. The V–O–Mn angle is 163.0°, which is slightly bent. The structural parameters of 2 is similar to that previously reported for 1 and 3, in which the M–O lengths are 1.964 Å and 2.087 Å, the \(V=O\) lengths are 1.640 Å and 1.658 Å and the V–O–M angles are 179.1° and 156.0°, respectively. A summary of structural parameters is included in Table 4.S6. The torsion angle of the oxido bridge in 2, which is defined by N-V-Mn-N, is 39.3°. This is significantly larger than in 1 (2.6°) or 3 (9.5°). The saddle inversion observed in 1\(^{36,37,48}\) is not seen in 2 or 3.\(^{35}\)

![Scheme 4.1](image)

Scheme 4.1 Molecule 2 is synthesized in anhydrous dichloromethane with equimolar (omtaa)\(V=O\) and Mn(TMP)SbF\(_6\).
Measurements of the temperature-dependent magnetic susceptibility and the variable-field magnetization were performed in order to determine the sign and magnitude of the exchange interactions between the oxido-bridged paramagnetic metal centers in 1-3. As depicted in Figure 4.2, the magnetic susceptibility (χ) is measured from 2-300 K under a constant magnetic field of 0.7 T. The product of molar magnetic susceptibility and temperature (χT) of species 1-3 increases monotonically to a maximum value at 50 K, 5 K and 40 K, respectively. The maximum χT value for 1-3 are found to be 5.7, 4.6 and 2.8 emu·K/mol, which are in agreement with the spin-only magnetic moments for paramagnetic centers with S = 2, 2.5 and 3, respectively. This is consistent with variable-field susceptibility measurements, where a fit of the Brillouin function (equation 4 in the SI) further confirms that the ground states of 1-3 have spin values of S = 2, 2.5 and 3, respectively. Application of an appropriate Van Vleck equation allows for the determination of J values for 1 (J_{exp} = +43 cm^{-1}), 2 (J_{exp} = +3 cm^{-1}) and 3 (J_{exp} = +37 cm^{-1}). Further experimental and fitting details are provided in the SI, specifically equations 2-3.

We therefore conclude that the magnetic interactions in 1-3 are dominated by ferromagnetic coupling between the paramagnetic centers. The magnitude of this exchange interaction in 2 is at least one order smaller than that of 1 and 3. Qualitatively, the magnitude of the J in the d^1-d^4 electronic configuration of 2 should be similar to that in the d^1-d^5 configuration of 3 (see Figure 4.S2). The additional unpaired electron in this d^1-d^5 system is localized in a d(x^2-y^2) orbital and therefore has only an insignificant contribution to the exchange interaction due to negligible orbital overlap between the d(x^2-y^2) orbitals of the metal centers.
Figure 4.2 Temperature-dependent magnetic susceptibility and variable-field magnetization (in-set) of 1-3. For comparison purposes, this data is not corrected for diamagnetic susceptibility. 1 has been previously reported.\textsuperscript{37}

In order to consider alternative explanations for the observed small $J$ in 2, such as the M–O–M bending angle or M–O bond lengths, we calculated the $J$ values for untwisted examples with similar electronic configurations as 1-3. We utilized a kinetic exchange model based on Anderson’s theory,\textsuperscript{31} corrected with an angular overlap model\textsuperscript{30} for oxido-bridged complexes as reported by Weihe and Güdel.\textsuperscript{29,32} According to this model, the kinetic exchange interaction is much larger than the potential exchange interaction in oxido-bridged complexes. Therefore, it is safe to ignore potential exchange contributions.\textsuperscript{29,32,47} The splitting of high- and low-spin states can therefore be understood as a kinetic exchange (also described as a second-order effect through virtual electron transfer between the metal ions) as described by Anderson.\textsuperscript{31} The kinetic
exchange interaction is caused by mixing of the single electron transfer excited states with the ground states. This allows for the derivation of a theoretical expression for J based on the electronic configuration and molecular symmetry of 1-3 (equations 15–17, Table 4.S1, Table 4.S2). Since the effective electron transfer integral $\tilde{h}_{ij}$ (i, j is an orbital representation such as $e_{\tilde{z}} \bar{z}, \zeta, \eta$ and $\theta$ from equation 9-14 in the SI and Figure 4.S3) can be related to the ligand field parameters using an angular overlap model (equation 18-22 in Table 4.S3) an angular dependent numerical expression of J for 1-3 with effective ligand field parameters can be determined (equation 23-25 in Table 4.S4).

Empirical values for the resulting effective ligand field parameters $x'$, $e_{\pi}'$, $e_{\sigma p}'$, $e_{\sigma s}'$ and $I'$ have been previously reported, and are summarized in Table 4.S5. The bending angle $\phi$ is defined by the angle of M–O–M (Table 4.1).

Using the empirical parameters (Table 4.S5) and the M–O–M angle $\phi$ (Table 4.1), a value for J can be computed for untwisted metallic complexes 1, $J_{\text{calc}} = +84 \text{ cm}^{-1} (d^1-d^3)$, 2, $J_{\text{calc}} = +87 \text{ cm}^{-1} (d^1-d^4)$ and 3, $J_{\text{calc}} = +72 \text{ cm}^{-1} (d^1-d^5)$. When compared with the experimental results for 1 ($J_{\text{exp}} = +43 \text{ cm}^{-1}$) and 3 ($J_{\text{exp}} = +37 \text{ cm}^{-1}$), we find a consistent 2 fold difference. We believe this systematic error is reasonable since the empirical effective ligand field parameters ($x'$, $e_{\pi}'$, $e_{\sigma p}'$, $e_{\sigma s}'$ and $I'$) were obtained using systems with similar M–O bond lengths in their oxido linkages (eg, M$_1$–O–M$_2$, M$_1$–O $\approx$ M$_2$–O $\approx 1.80$ Å,), while in 1-3 the oxido bridge is highly unsymmetric, with a significantly shorter V≡O bond vs. the M–O bond (eg, V≡O–M, V≡O $\approx 1.65$ Å, M–O $\approx 2.05$ Å). The magnitude of J has been shown to decrease exponentially with an increase of the longer M–O bond. If J is normalized (Figure 4.S4), the relative magnitude of $J_{\text{calc}}$ and $J_{\text{exp}}$ in 1 and 3 are similar. Therefore, we propose that these equations can be used
to establish a calculated J value for 2 in an otherwise untwisted geometry. The
calculation ($J_{\text{calc}} = +87 \text{ cm}^{-1}$) is significantly larger than the observed ($J_{\text{exp}} = +3 \text{ cm}^{-1}$)
for 2 (Figure 4.1, S4 and Table 4.1), suggesting that an additional parameter is necessary
to accurately describe the magnetic coupling in 2.

**Table 4.1** Selected structural parameters and J values for 1-3.

<table>
<thead>
<tr>
<th>#</th>
<th>V-O-M(°)</th>
<th>Torsion(°)</th>
<th>$J_{\text{calc}}$ (cm$^{-1}$)</th>
<th>$J_{\text{exp}}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>179.1</td>
<td>2.6</td>
<td>+84</td>
<td>+43</td>
</tr>
<tr>
<td>2</td>
<td>163.0</td>
<td>39.3</td>
<td>+87</td>
<td>+3</td>
</tr>
<tr>
<td>3</td>
<td>166.0</td>
<td>9.5</td>
<td>+72</td>
<td>+37</td>
</tr>
</tbody>
</table>

The most striking structural difference between 1, 2 and 3 is the unusual twisting
graph observed between the individual ligand planes of 2. Since the kinetic
exchange interaction relies upon electronic coupling between the two spin centers,
(equation 9-14) overlap between the magnetic orbitals is necessary for such interactions
to occur. The observed twist in 2 should therefore result in smaller magnetic coupling
between the two paramagnetic metal sites. As can be seen in Figure 4.3A, we propose
that the oxygen atom p$_\pi$ orbitals are coupled to the geometry at the vanadium center due
to the multiple bond character of V═O, and thus will rotate with the vanadium center
as the oxido bridge twists. This yields a d$_\pi$-p$_\pi$ mismatch between the oxygen p$_\pi$ orbitals
and the corresponding manganese d$_\pi$ orbitals. Due to the degeneracy of d$_\pi$ and p$_\pi$, this
influence of this twist will minimize the d$_\pi$-p$_\pi$ overlap as the torsion angle approaches
$45^\circ$. Unbalanced mixing of the bridging orbitals to metal centers appears to be necessary to observe this effect, since we are unable to identify the impact of torsion in any of the previously known twisted oxido/hydroxide-bridged bimetallic species. (Table 4.S8)

Although the twisted linkage of 2 was unexpected, a comparison of the X-ray crystal structures reveals the origin of this structural feature. Tetraazacyclotetradecine (tmtaa or omtaa) ligands are capable of undergoing a structural isomerization, with metal complexes exhibiting both wing-up$^{34}$ and wing-down$^{36}$ geometries.$^{35, 37}$ As shown in Figure 4.3B, the wing-down geometry has fewer possible steric interactions when bound to a Lewis acid since the phenyl rings point away from the bridged V═O−M. The other structural isomer, wings-up, has the phenyl group directed toward the Lewis acid. When interacting with a chromium porphyrin as in 1, the wing-down configuration is more stable since it has less steric repulsion with its relatively short Cr−O bond. If the M−O bond is too weak to allow the wing-down geometry to be thermodynamically accessed, the resulting wing-up configuration will twist in order to minimize the steric interactions as observed in 2. We suggest that such structural isomerism is an additional synthetic strategy for utilizing torsion angles to tune exchange coupling between paramagnetic centers. Other synthetic strategies have been reported that use torsion angles to modify p$_\pi$-p$_\pi$ overlap,$^{45}$ which may also be applicable for influencing d$_\pi$-p$_\pi$ overlap.
Figure 4.3 (A) Schematic illustration of torsion effects on exchange coupling between two metallic sites. The d_π-p_π overlap is minimal at a torsion degree of 45°. (B) The wing-up and wing-down configurations of (omtaa)V═O. This results in disparate steric hindrances and is the origin of the twisted geometry in 2.
4.4 Conclusions

Our results show that Anderson’s kinetic exchange interaction model is sufficient for rationalizing the sign and magnitude of J. Since the magnetic orbitals of 2 obey the strictly orthogonality rules proposed by Kahn\textsuperscript{24–26,28} even when in its twisted configuration, the small J value observed suggests that the potential exchange interaction is negligible. Therefore, consideration of the appropriate kinetic interactions is required for a fundamental understanding of the magnetic coupling in such linkage.

In summary, we have prepared the first example of d\textsuperscript{1}-d\textsuperscript{4} heterobimetallic oxido-bridged V–O–Mn complex and demonstrate that a molecular twist can significantly alter the magnitude of ferromagnetic coupling between paramagnetic metal centers, in this case d\textsuperscript{4} Mn(II) and d\textsuperscript{1} V(IV). This result confirms that ferromagnetic coupling in such heterobimetallic molecules can be explained using a kinetic exchange model\textsuperscript{29,31,50} where the magnitude of magnetic interactions are determined by the amount of orbital overlap between the paramagnetic sites. Therefore, this work represents a step forward in understanding and modelling all of the interactions that participate in magnetic coupling between paramagnetic centers. In particular, the ability to tune d_{\sigma}-p_{\pi} overlap using a simple geometric twist through a single atom is a potentially powerful new method for influencing magnetic and electronic coupling across the shortest of bridges.

We believe that this result, coupled with known importance of p_{\pi}-p_{\pi} overlap\textsuperscript{44–46} suggests a general mechanism for utilizing molecular geometries to modify the properties of systems with coupled spins, including those dominated by p_{\pi}-p_{\pi}, d_{\sigma}-p_{\pi} and d_{\pi}-d_{\pi} interactions. The influence of such twisting geometries on the bridging orbitals
will need to be considered when designing next-generation, molecule-based systems that rely upon metal-metal interactions to improve performance.

4.5 Supporting information

Experimental details

General Procedures.

All reactions were performed under an atmosphere of nitrogen in an Innovative Technology glovebox or using Schlenk techniques. All chemicals were purchased from VWR International, Sigma Aldrich, Alfa Aesar or TCI America and used without further purification. All solvents were stored over 4Å molecular sieves prior to use. Dichloromethane and pentane were sparged with N₂ and dried over an alumina column using the method of Grubbs. Toluene was dried over purple sodium benzophenone ketyl, then vacuum transferred and freeze-pump-thawed before storing in Teflon-sealed Schlenk bombs. Acetonitrile was dried over CaH₂ and distilled prior to use. Absorption spectra were recorded on an Olis RSM-1000 spectrometer using 1 cm Teflon-sealed quartz cuvettes. Attenuated total reflectance (ATR)-FTIR spectra were recorded with Bruker Alpha ATR-FTIR infrared spectrometer equipped with a Platinum™ Diamond ATR attachment. Magnetic susceptibilities were measured on a Quantum Design MPMS-XL7 SQUID Magnetometer. A saturation plot was measured at 2 K with the applied field being varied from 0~70000 oe. Temperature-dependent magnetic susceptibilities were performed from 2-300 K. The reported errors of fits for magnetic data were obtained from two separate measurements. Crystalline samples (ca. 10-30 mg) were loaded into gelcap/straw sample holders and mounted to the sample rod with Kapton tape for temperature-dependent measurements.
The ligands studied in this report are represented by the following abbreviations: TMP, tetrakis((4-methoxyl)phenyl)porphyrin; TFMP, tetrakis((4-trifluoromethyl)phenyl)porphyrin; tmtaa: 7,16-dihydro-6,8,15,17-tetramethylidibenz[b,i][1,4,8,11]tetaazacyclotetradecine, omtaa: 7,16-dihydro-6,8,11,12,15,17,20,21-octamethylidibenz[b,i][1,4,8,11]tetaazacyclotetradecine. The ligands are synthesized according to the reports of Weare and coworkers and Goedken and coworkers.\textsuperscript{52} compound 1,\textsuperscript{37} \textsuperscript{35} and (omtta)V═O\textsuperscript{52} are synthesized as previously reported.

X-Ray crystallography

Crystals were mounted on MiTeGen mounts and cooled to 100 K. X-ray intensity data were measured on a Bruker-Nonius X8 Kappa APEX II system equipped with a graphite monochromator and a MoK\ensuremath{\alpha} fine-focus sealed tube ($\lambda = 0.71073 \text{ Å}$). Unit cell dimensions were determined from symmetry constrained fits of the reflections. Frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the multi-scan method (SADABS). Structures were solved using direct methods (Bruker XS) and refined using the Bruker SHELX 2013\textsuperscript{53} software package using full-matrix least-squares refinement on F. All non-hydrogen atoms were identified in the original solution, or located from the difference map from refinement results. Hydrogen atoms were placed at idealized positions and allowed to ride on the nearest non-H atom. Fig.s of the molecular structures were created using Olex\textsuperscript{2} Crystallographic information files for all structures are available in the ESI\textsuperscript{†} and from the Cambridge Crystallographic Data Center (www.ccdc.cam.ac.uk). CCDC reference number: 2 (1453972)
Synthesis of Mn(TMP)SbF<sub>6</sub>

The synthesis is adapted from a previous publication. In the glovebox, Mn(TMP)Cl (230.0 mg, 0.28 mmol) and NaSbF<sub>6</sub> (81.0 mg 0.31 mmol) were added to 8 mL of a 1:1 acetonitrile : toluene mixture in a 50 mL Teflon-sealed Schlenk flask and heated at 80 °C for 12 h. The solution was then cooled slowly to room temperature and was filtered to remove NaCl. A fine green powder was obtained from the filtrate after removal of the solvent in vacuo. The final product was obtained after recrystallization via layered diffusion of pentane (15 mL) into a dichloromethane (3 mL) solution at -25 °C. MnSbF<sub>6</sub>TMP (2). Yield: 260.5 mg, 90.9%. Anal. calc’d for C<sub>48</sub>H<sub>36</sub>F<sub>6</sub>MnN<sub>4</sub>O<sub>4</sub>Sb•2CH<sub>2</sub>Cl<sub>2</sub>: C, 50.32; H, 3.38; N, 4.69. Found: C, 50.24; H, 3.32; N, 4.81. HRMS-ESI (M<sup>+</sup>) calc’d for C<sub>48</sub>H<sub>36</sub>MnN<sub>4</sub>O<sub>4</sub>: 787.2112, Found. 787.2086

Synthesis of (omtaa)V═O→Mn(TMP)SbF<sub>6</sub> (2)

In the glovebox, (omtaa)V═O (14.0 mg, 0.03 mmol) and Mn(TMP)SbF<sub>6</sub> (30.7 mg 0.03 mmol) were dissolved in 5 mL dichloromethane in a 20 mL glass vial and stirred at room temperate for 5 min. A small amount of solution was dropped onto a FT-ATR sample holder and allow dry. The IR spectrum was then taken from this dried sample to monitor the reaction completeness using the disappearance of ν<sub>V═O</sub> at 972 cm<sup>-1</sup>. When reaction is complete, 15 ml pentane was slowly added onto this solution and stored in a -20 °C freezer for three days. Green crystalline solid was obtained after filtration. The final X-ray quality product was obtained after recrystallization via layered diffusion of pentane (2.5 mL) into a dichloromethane (1 mL) solution with 4 mg sample at -20 °C. Yield after recrystallization: 29.5 mg, 66.0%. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>) λ<sub>max</sub> (nm) (ε (M<sup>-1</sup>cm<sup>-1</sup>)), 330 (34000), 379 (46750), 398 (46320), 485 (29750), 524 (5040), 578 (6500), 618 (8520). ATR/FTIR ν<sub>V═O</sub> (cm<sup>-1</sup>): 898(s). Anal. calc’d for
C\textsubscript{74}H\textsubscript{66}F\textsubscript{6}MnN\textsubscript{8}O\textsubscript{5}SbV•CH\textsubscript{2}Cl\textsubscript{2}: C, 57.23; H, 4.35; N, 7.12. Found: C, 57.43; H, 4.32; N, 7.31.

HRMS-ESI (M\textsuperscript{+}) calc’d for C\textsubscript{74}H\textsubscript{66}MnN\textsubscript{8}O\textsubscript{5}V: 1252.3971. Found 1252.3947.

**X-ray Crystallography**

![X-ray crystal structure of 2](image)

**Figure 4.S1.** X-ray crystal structure of 2. Thermal ellipsoids are drawn at 50% probability. Anion, hydrogen atoms and solvent molecules are omitted for clarity.

A dark black block-like specimen of C\textsubscript{78}H\textsubscript{74}Cl\textsubscript{8}F\textsubscript{6}MnN\textsubscript{8}O\textsubscript{5}SbV, approximate dimensions 0.725 mm × 0.322 mm × 0.221 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

A total of 1579 frames were collected. The total exposure time was 19.85 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 162410 reflections to a maximum θ angle of 27.877° (0.76 Å resolution), of which 20279 were independent (average redundancy 5.61, completeness = 99.9 %, R\textsubscript{int} = 3.92%, R\textsubscript{sig} = 2.52%) and 16834 (83.01%) were greater than 2σ(F\textsuperscript{2}). The final cell constants of a = 16.1779(6) Å, b = 17.0517(7) Å, c =
17.8263(7) Å, α = 116.513(2)°, β = 96.514(2)°, γ = 98.825(2)°, volume = 4255.3(3) Å³, are based upon the refinement of the XYZ-centroids of 9643 reflections above 20 σ(I) with 4.592° < θ < 56.732°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.7732.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P-1, with Z = 2 for the formula unit, C₇₈H₇₄Cl₈F₆Mn₈N₈O₅SbV. The final anisotropic full-matrix least-squares refinement on F² with 1044 variables converged at R₁ = 6.12 %, for the observed data and wR₂ = 17.46 % for all data. The goodness-of-fit was 1.084. The largest peak in the final difference electron density synthesis was 1.793 e/Å³ and the largest hole was -1.117 e/Å³ with an RMS deviation of 0.138 e/Å³. On the basis of the final model, the calculated density was 1.427 g/cm³ and F(000), 1854.0 e⁻.

SQUEEZE of PLATON was applied to deal with disordered solvent. Analysis revealed 512 cubic angstroms of void space and 211 electrons housed therein. This approximates to 5 CH₂Cl₂ per unit cell, or 2.5 per formula unit.

Magnetic Data

\[ \hat{H}_{12} = -2JS_1S_2 \]  

\[ \chi = \frac{\chi_M}{1 - \left( \frac{2J}{N_A \mu_B g^2} \right) \chi_M} \]

\[ \chi_M = \frac{NB^2g^2}{3k_B(T-\theta)} \left( \frac{30 + 105e^{\frac{5J}{k_BT}}}{8 + 12e^{\frac{5J}{k_BT}}} \right) + C \]

\[ \chi_M = \frac{NB^2g^2}{3k_B(T-\theta)} \left( \frac{30g_1^2 + 84g_2e^{\frac{6J}{k_BT}}}{(5 + 7e^{\frac{6J}{k_BT}})} \right) + C, \quad g_1 = \frac{7g_{Mn} - g_v}{6}, \quad g_2 = \frac{5g_{Mn} + g_v}{6} \]
\[ \frac{M}{N\mu_B} = gSB_0(x) \]

\[ B_0(x) = \frac{2S + 1}{2S} \coth\left(\frac{2S + 1}{2S} \times \frac{g\mu_B S}{k_B \times T}\right) - \frac{1}{2S} \coth\left(\frac{1}{2S} \times \frac{g\mu_B S}{k_B \times T}\right) \]

In order to determine the exact value of the magnitude of exchange interaction for 2 and 3, we applied a simple isotropic spin Hamiltonian (equation 1) to fit the data (Figure 4.2). The final expressions (equations 2 and 3) are derived from the Van Vleck equation\(^{23}\) where \( N \) is Avogadro's number, \( k_B \) is the Boltzmann constant, \( T \) is the temperature, \( \beta \) is the Bohr magneton, \( g \) is the electron g-factor, \( \theta \) is the Weiss constant, \( C \) represents the total contribution of temperature-independent-paramagnetic susceptibility (TIP) and diamagnetic susceptibility and \( J \) corresponds to the net magnetic interaction between paramagnetic centers. Effects of zero-field-splitting, spin-orbital coupling, intermolecular interactions and experimental error are reflected in the small differences of the fit value for \( g \). The magnetic detail of 1 has been previously determined.\(^{37}\) A mean-field approximation (equation 3) is used to increase the fit quality for 2. The asymmetrical contribution in the \( g \) factor is taken into consideration for 3 (equation 4). This additional treatment didn’t influence the \( J \) value significantly. However, including this treatment allows a slight improvement in fit.

Using the equation (2) for 2, the values \( J = +2.6 \pm 0.1 \text{ cm}^{-1}, \theta = -0.33 \pm 0.01 \text{ K}, g = 1.91, C = -3.05 \pm 0.24 \times 10^{-3} \text{ emu/mol and } zJ' = +0.054 \pm 0.019 \text{ cm}^{-1} \) with \( R^2 = 0.9852 \) were computed.

Using the equation (3) for 3, the values \( J = +37.3 \pm 1.9 \text{ cm}^{-1}, \theta = -0.27 \pm 0.03 \text{ K}, g_{Mn} = 1.90 \pm 0.01 \text{ and } g_v = 2.02 \pm 0.01 \text{ and } C = -8.75 \pm 0.63 \times 10^{-4} \) with \( R^2 = 0.9964 \) were computed.
Electronic configurations for 1-3

Figure 4.52. Schematic demonstration of the electronic configurations for 1-3.
Details for the empirical computation of J

### Table 4.S1. Expressions for the kinetic exchange interaction of J

<table>
<thead>
<tr>
<th>Interaction Type(^a)</th>
<th>Expression(^b,c)</th>
<th>Label</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\frac{1}{2})<em>(A) (\rightarrow) (\frac{1}{2})</em>(B)</td>
<td>(- \frac{1}{n_A n_B} \frac{h_{ij}^2}{U})</td>
<td>(5)</td>
</tr>
<tr>
<td>(\frac{1}{2})_(A) (\rightarrow) ([0]_B)</td>
<td>(+ \frac{1}{n_A} \frac{h_{ij}^2}{U} \frac{I}{U})</td>
<td>(6)</td>
</tr>
<tr>
<td>([1]<em>A) (\rightarrow) (\frac{1}{2})</em>(B)</td>
<td>(+ \frac{1}{n_B} \frac{h_{ij}^2}{U} \frac{I}{U})</td>
<td>(7)</td>
</tr>
<tr>
<td>([1]_A) (\rightarrow) ([0]_B)</td>
<td>(- \frac{(n_A - n_B)}{(n_A + 1)(n_B + 1)} \frac{h_{ij}^2}{U} \frac{I}{U})</td>
<td>(8)</td>
</tr>
</tbody>
</table>

\(^a\) Interaction type represents the virtual electron transfer from site A to site B. For example, the half to half transfer \((\frac{1}{2}\)_\(A\) \(\rightarrow\) \(\frac{1}{2}\)_\(B\)) represents the process which transfers one electron from A to an orbital on B, which then pairs up in the orbital on B. This electron transfer process would result the formation of low spin excited state, which is represented by the negative sign in this expression.

\(^b\) The original expressions are based on \(\hat{H}_{ab} = +J_{ab}\hat{S}_a \hat{S}_b\), while we use \(\hat{H}_{ab} = -2J_{ab}\hat{S}_a \hat{S}_b\). The “-2” fold difference is applied in the final expressions.

\(^c\) \(n_A\) and \(n_B\) stand for the number of unpaired electrons, \(h_{ij}\) is the transfer integral (see Figure 4.S2 for detail) and \(U\) is the energy required for this electron transfer to occur.
\[ h_{\zeta\zeta} = \langle \zeta_a | \hat{V}_{AB} | \zeta_b \rangle = \langle \zeta_b | \hat{V}_{AB} | \zeta_a \rangle \quad (9) \]

\[ h_{\eta\eta} = \langle \eta_a | \hat{V}_{AB} | \eta_b \rangle = \langle \eta_b | \hat{V}_{AB} | \eta_a \rangle \quad (10) \]

\[ h_{\zeta\xi} = \langle \xi_a | \hat{V}_{AB} | \xi_b \rangle = \langle \xi_b | \hat{V}_{AB} | \xi_a \rangle \quad (11) \]

\[ h_{\epsilon\epsilon} = \langle \epsilon_a | \hat{V}_{AB} | \epsilon_b \rangle = \langle \epsilon_b | \hat{V}_{AB} | \epsilon_a \rangle \quad (12) \]

\[ h_{\theta\theta} = \langle \theta_a | \hat{V}_{AB} | \theta_b \rangle = \langle \theta_b | \hat{V}_{AB} | \theta_a \rangle \quad (13) \]

\[ h_{\eta\theta} = \langle \eta_a | \hat{V}_{AB} | \theta_b \rangle = \langle \theta_b | \hat{V}_{AB} | \eta_a \rangle \quad (14) \]

**Figure 4.S3.** Schematic illustration of important one-electron transfer integrals. The transfer integrals \( h_{\zeta\zeta}, h_{\xi\xi}, h_{\eta\eta}, h_{\theta\theta} \) and \( h_{\eta\theta} \) are shown using double arrows.

**Table 4.S2.** Theoretical \( J \) values for electronic configurations of 1-3

<table>
<thead>
<tr>
<th>m,n</th>
<th>( d^m )</th>
<th>( d^n )</th>
<th>( J_{calc.a,b} )</th>
<th>Label</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,3</td>
<td>( \zeta )</td>
<td>( \zeta\eta\zeta )</td>
<td>(-\frac{2}{3}h'<em>{\zeta\zeta} + \frac{1}{3}h'</em>{\eta\eta}I' + \frac{1}{3}h'<em>{\xi\xi}I' + \frac{1}{3}h'</em>{\theta\theta}I')</td>
<td>(15)</td>
</tr>
<tr>
<td>1,4</td>
<td>( \zeta )</td>
<td>( \zeta\eta\zeta\theta )</td>
<td>(-\frac{1}{2}h'<em>{\zeta\zeta} + \frac{1}{4}h'</em>{\eta\eta}I' + \frac{1}{4}h'<em>{\xi\xi}I' + \frac{1}{4}h'</em>{\theta\theta}I' + \frac{1}{4}h'_{\eta\theta}I')</td>
<td>(16)</td>
</tr>
<tr>
<td>1,5</td>
<td>( \zeta )</td>
<td>( \zeta\eta\zeta\eta\epsilon )</td>
<td>(-\frac{2}{5}h'<em>{\zeta\zeta} + \frac{1}{5}h'</em>{\eta\eta}I' + \frac{1}{5}h'<em>{\xi\xi}I' + \frac{1}{5}h'</em>{\eta\theta}I' + \frac{1}{5}h'_{\theta\theta}I')</td>
<td>(17)</td>
</tr>
</tbody>
</table>

\(^a\) due to \( U \) being unknown, the effective parameters \( \frac{h_{ij}^2}{U} = \hat{h}_{ij} \) and \( \frac{I}{U} = I' \) are used

\(^b\) expressions are derived from the one-electron transfer integrals: equation 5-8.
Table 4.S3. Angular-dependent ligand field parameters used in the transfer integrals.\textsuperscript{29,32}

<table>
<thead>
<tr>
<th>Equations</th>
<th>Label</th>
</tr>
</thead>
<tbody>
<tr>
<td>$h_{\eta\phi}(\phi) = \sqrt{e_\pi e_{\text{op}}}(\sin(\phi))$</td>
<td>(18)</td>
</tr>
<tr>
<td>$h_{\theta\phi}(\phi) = e_\alpha + e_{\text{op}}(\cos(\phi))$</td>
<td>(19)</td>
</tr>
<tr>
<td>$h_{\eta\gamma}(\phi) = e_\pi (-\cos(\phi))$</td>
<td>(20)</td>
</tr>
<tr>
<td>$h_{\phi\pi}(\phi) = e_\pi$</td>
<td>(21)</td>
</tr>
<tr>
<td>$h_{\phi\nu}(\phi) = x(180 - \phi)$</td>
<td>(22)</td>
</tr>
</tbody>
</table>

Table 4.S4. Theoretical $J$ values based on angular-dependent ligand field parameters for 1-3

<table>
<thead>
<tr>
<th>#</th>
<th>$J_{\text{calc}}^{a,b}$</th>
<th>Label</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$-\frac{2}{3} x^2 (180 - \phi)^2 + \frac{1}{3} e_\pi^2 \cos^2(\phi)I' + \frac{1}{3} e'<em>\pi^2 I'' + \frac{1}{3} e'</em>{\text{op}} e''_{\text{op}} \sin^2(\phi)I'$</td>
<td>(23)</td>
</tr>
<tr>
<td>2</td>
<td>$-\frac{1}{2} x^2 (180 - \phi)^2 + \frac{1}{4} e_\pi^2 \cos^2(\phi)I' + \frac{1}{4} e'<em>\pi^2 I'' + \frac{1}{4} e'</em>{\text{op}} e''<em>{\text{op}} \sin^2(\phi)I' + \frac{1}{4} (e'</em>\alpha + e'_{\text{op}} \cos(\phi))^2 I'$</td>
<td>(24)</td>
</tr>
<tr>
<td>3</td>
<td>$-\frac{2}{5} x^2 (180 - \phi)^2 + \frac{1}{5} e_\pi^2 \cos^2(\phi)I' + \frac{1}{5} e'<em>\pi^2 I'' + \frac{1}{5} e'</em>{\text{op}} e''<em>{\text{op}} \sin^2(\phi)I' + \frac{1}{5} (e'</em>\alpha + e'_{\text{op}} \cos(\phi))^2 I'$</td>
<td>(25)</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The effective parameters: $\frac{e_\pi}{\sqrt{U}} = e'_\pi$, $\frac{e_{\text{op}}}{\sqrt{U}} = e'_{\text{op}}$, $\frac{e'_\pi}{\sqrt{U}} = e''_\pi$, $\frac{x}{\sqrt{U}} = x'$, $\frac{I}{U} = I'$ are used

\textsuperscript{b} A graphical presentation of these equations can be seen in Weihe and Güdel’s previous work.\textsuperscript{32}
Table 4.S5. Previously reported empirical effective parameters.\textsuperscript{32}

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x'$</td>
<td>0.19</td>
</tr>
<tr>
<td>$l'$</td>
<td>0.29</td>
</tr>
<tr>
<td>$e'_{\pi}$</td>
<td>20.86</td>
</tr>
<tr>
<td>$e'_{es}$</td>
<td>18.42</td>
</tr>
<tr>
<td>$e'_{op}$</td>
<td>39.46</td>
</tr>
</tbody>
</table>

$I'$ is dimensionless. $e'_{\pi}$, $e'_{es}$, $e'_{op}$ and $x'$ are in units of (cm$^{-1}$)$^{1/2}$

Table 4.S6. Summary of selected structural parameters and J values for 1-3

<table>
<thead>
<tr>
<th>#</th>
<th>System</th>
<th>V-O (Å)</th>
<th>M-O (Å)</th>
<th>V-O-M (°)</th>
<th>Torsion (°)</th>
<th>$J_{\text{calc}}$ (cm$^{-1}$)</th>
<th>$J_{\text{exp}}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>d$^1$-d$^4$ Cr(III)-V(IV)</td>
<td>1.640</td>
<td>1.964</td>
<td>179.1</td>
<td>2.6</td>
<td>+84</td>
<td>+42.5</td>
</tr>
<tr>
<td>2</td>
<td>d$^1$-d$^4$ Mn(III)-V(IV)</td>
<td>1.654</td>
<td>2.080</td>
<td>163.0</td>
<td>39.3</td>
<td>+87</td>
<td>+2.6</td>
</tr>
<tr>
<td>3</td>
<td>d$^1$-d$^5$ Mn(II)-V(IV)</td>
<td>1.658</td>
<td>2.087</td>
<td>157.0</td>
<td>9.3</td>
<td>+72</td>
<td>+37.3</td>
</tr>
</tbody>
</table>
Figure 4.S4. Normalized comparison of $J_{\text{calc}}$ and $J_{\text{exp}}$ for 1-3

Electronic absorption and solid state ATR-FTIR spectra of 2
Figure 4.5. Molar absorptivity (in dichloromethane) and solid state ATR-FTIR spectra of 2.
Figure 4.S6. Comparison of $\nu_{V=O}$ of (omtaa)V=O and 2.
HRMS-ESI results of 2 including simulated patterns for \([M]^+\).

**Figure 4.S7.** HRMS-ESI and simulated patterns of \([M]^+\) for 2
### Additional Tables

**Table 4.S7. Crystal data and structure refinement details for 2**

<table>
<thead>
<tr>
<th>Identification</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ccdc number</td>
<td>1453972</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C_{78}H_{74}Cl_{8}Mn_{8}O_{5}SbV</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1828.68</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>100.08</td>
</tr>
<tr>
<td>Crystal system</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P -1</td>
</tr>
<tr>
<td>a/Å</td>
<td>16.1799(6)</td>
</tr>
<tr>
<td>b/Å</td>
<td>17.0517(7)</td>
</tr>
<tr>
<td>c/Å</td>
<td>17.8263(7)</td>
</tr>
<tr>
<td>α/°</td>
<td>116.513(2)</td>
</tr>
<tr>
<td>β/°</td>
<td>96.514(2)</td>
</tr>
<tr>
<td>γ/°</td>
<td>98.825(2)</td>
</tr>
<tr>
<td>Volume/Å³</td>
<td>4255.3(3)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>ρ_cal/cm³</td>
<td>1.427</td>
</tr>
<tr>
<td>μ/mm⁻¹</td>
<td>0.885</td>
</tr>
<tr>
<td>F(000)</td>
<td>1854.0</td>
</tr>
<tr>
<td>Crystal size/mm³</td>
<td>0.725 × 0.322 × 0.221</td>
</tr>
<tr>
<td>Radiation</td>
<td>MoKα (λ = 0.71073)</td>
</tr>
<tr>
<td>2Θ range for data collection/°</td>
<td>2.608 to 55.754</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-21 ≤ h ≤ 21, -22 ≤ k ≤ 22, -23 ≤ l ≤ 23</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>162410</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>16834 [R_{int} = 0.0392, R_{sigma} = 0.0252]</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>20279/0/1044</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.084</td>
</tr>
<tr>
<td>Final R indexes [I&gt;2σ (I)]</td>
<td>R₁ = 0.0612, wR₂ = 0.1612</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>R₁ = 0.0768, wR₂ = 0.1746</td>
</tr>
<tr>
<td>Largest diff. peak/hole / e Å⁻³</td>
<td>1.793/-1.117</td>
</tr>
</tbody>
</table>
Table 4.8. Previously reported oxido-bimetallic species with torsion angles.

<table>
<thead>
<tr>
<th>CCDC Refcode</th>
<th>System</th>
<th>V-O (Å)</th>
<th>M-O(Å)</th>
<th>V-O-M(°)</th>
<th>Torsion(°)</th>
<th>$J_{\text{exp}}$ (cm$^{-1}$)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>HEDTT</td>
<td>d$^3$-d$^5$ Cr(III)-O-Fe(III)</td>
<td>1.774</td>
<td>1.760</td>
<td>176.5</td>
<td>9.4</td>
<td>-150</td>
<td>48</td>
</tr>
<tr>
<td>LAQNOG</td>
<td>d$^3$-d$^5$ Cr(III)-O-Fe(III)</td>
<td>1.775</td>
<td>1.751</td>
<td>177.7</td>
<td>29.9</td>
<td>-150</td>
<td>54</td>
</tr>
<tr>
<td>HETHIN</td>
<td>d$^3$-d$^5$ Fe(III)-O-Fe(III)</td>
<td>1.7918</td>
<td>1.7918</td>
<td>180.0</td>
<td>7.1</td>
<td>-116</td>
<td>43</td>
</tr>
<tr>
<td>FESZEI</td>
<td>d$^3$-d$^5$ Fe(III)-O-Fe(III)</td>
<td>1.759</td>
<td>1.759</td>
<td>176.1</td>
<td>30.3</td>
<td>-129</td>
<td>39</td>
</tr>
<tr>
<td>WIHSAH</td>
<td>d$^3$-d$^5$ Fe(III)-O-Fe(III)</td>
<td>1.785</td>
<td>1.785</td>
<td>174.7</td>
<td>27.1</td>
<td>-116</td>
<td>49</td>
</tr>
<tr>
<td>KETBOB</td>
<td>d$^4$-d$^4$ Mn(III)-O-Mn(III)</td>
<td>1.751</td>
<td>1.757</td>
<td>168.5</td>
<td>26.0</td>
<td>-120</td>
<td>40</td>
</tr>
<tr>
<td>CAZNEX</td>
<td>d$^4$-d$^4$ Mn(III)-O-Mn(III)</td>
<td>1.789</td>
<td>1.789</td>
<td>173.0</td>
<td>16.2</td>
<td>-115.8</td>
<td>55</td>
</tr>
<tr>
<td>ZOVRH</td>
<td>d$^4$-d$^4$ Mn(III)-OH-Mn(III)</td>
<td>2.041</td>
<td>2.015</td>
<td>159.8</td>
<td>29.9</td>
<td>-37</td>
<td>41</td>
</tr>
<tr>
<td>ZEKUTE</td>
<td>d$^4$-d$^4$ Mn(III)-OH-Mn(III)</td>
<td>1.998</td>
<td>2.024</td>
<td>152.7</td>
<td>4.3</td>
<td>-30.5</td>
<td>42</td>
</tr>
</tbody>
</table>

4.6 Acknowledgements

This work was supported by generous startup funding from North Carolina State University. We acknowledge Dr. Daniel Stasiw and Prof. David A. Shultz for assistance
in collecting SQUID data. Mass spectra were obtained at the NCSU Department of Chemistry Mass Spectrometry Facility.

4.7 References


CHAPTER 5

Phenoxido-Bridged Heterometallic Mn(II)-V(IV) Complexes: Synthesis, Structural Characterization, Magnetic and Electronic Property

This manuscript is prepared to submit to Inorg. Chem.

Tao Huang, Xinyuan Wu, Natalie T. Rice, Walter W. Weare and Roger D. Sommer

Huang, T performed all general characterization and magnetization work. He worked with Sommer, R. D. to conduct X-ray diffraction experiment. The synthesis was performed by

Huang, T, Natalie T. Rice and Wu, X.

Department of Chemistry, North Carolina State University;

Raleigh, NC, 27695-8204
5.1 Abstract

3-carboxylic acid substituted Schiff base ligands \((\text{L}_1-\text{L}_4)\) are prepared to support phenoxido-bridged heterometallic complexes containing \(\text{d}^5\) Mn(II) and \(\text{d}^1\) V(IV). Increasing the steric hindrance on the ethylene backbone is found to alter the thermodynamically favored coordination position of V(IV) from the inner \(\text{N}_2\text{O}_2\) site (1 and 2) to the outer \(\text{O}_2\text{O}_2\) site (3 and 4). Complexation of Mn(II) to the \(\text{O}_2\text{O}_2\) sites of 2 forms heterometallic complex 5, which has a poly-molecular chain structure as demonstrated by HR-ESI-MS. A monomeric complex 6 is obtained when chelating Mn(II) into the \(\text{N}_2\text{O}_2\) site of 4 and has been structurally characterized by X-ray crystallography. This Mn(II) center displays a tetragonal base-trigonal base, seven coordinate geometry, which represents the first manganese complex in this unusual ligand enviroment. When compared to the previously reported ferromagnetically coupled Mn(II)–O–V(IV) complex \(\text{Mn–O–V}\) \((J = +37 \text{ cm}^{-1}, H = -2J\hat{S}_\text{V} \cdot \hat{S}_\text{Mn})\) with a slightly bent geometry \((\text{Mn–O–V} = 156^\circ, \text{Mn–V} = 3.66 \text{ Å})\), the paramagnetic centers of 6 are antiferromagnetically coupled with \(J = -5 \text{ cm}^{-1}\). We propose that this change in \(J\) is due to the structural differences between the bridging linkages of \(\text{Mn–O–V}\) and 6, with Mn(II) and V(IV) in 6 being connected through a bis(phenoxido) bridge that has both a shorter bond distance and significantly more bent geometry \((\text{Mn–O–V} = 102.3^\circ, \text{Mn–V} = 3.24 \text{ Å})\). This result demonstrates that the sign of magnetic coupling between heterobimetallic centers can be manipulated through careful selection of bridging geometries.

5.2 Introduction

Binuclear complexes stabilized by ligand containing Schiff bases have a long and rich histroy.\(^1-8\) Due its synthetic simplicity and easily modifiable framework, this ligand set has been utilized in a wide variety of research topics including bimetallic bifunctional catalysis,\(^9-\)
biological enzymatic modeling and magnetic materials. 3-carboxylic acid substituted Schiff bases which derive from 3-formylsalicylic acid represent a well-studied frameworks for binuclear complexes (Schme 5.1). Complexes based on these ligands have been used to formulate the fundamental theories of magnetic coupling and magneto-structural relationship. Bimetallic systems based on such ligand sets such as Cu(II)V(IV), Cu(II)Cr(II), Cu(II)Fe(III), Cu(II)Ni(II) and Cu(II)Cu(II) which are important experimental systems which support and justify the quantum mechanics basis of molecular magnetism. A useful feature of the bis(phenoxido) linkage is that it can force two disparate metal ions into a rigid geometry with a close metal-metal distance. This increases intermetallic electronic coupling and results in models for studying magnetic interactions and charge transfer in polymetallic systems. However, heterobimetallic complexes composed entirely of early 3d transition metals ions (eg: Sc, Ti, V, Cr, Mn) remain structurally unknown, most likely due to their relatively large ion sizes that make it difficult for them to fit into the binding pockets of this ligand framework.

Herein, we describe the first example of structurally characterized bis(phenoxido)-bridged heterometallic complex containing V(IV) and Mn(II). The magnetic and electronic coupling between d\(^1\) V(IV) and d\(^5\) Mn(II) are quantified using magnetization measurements and cyclic voltammetry, which reveal important information about the interactions between early transition metals that are held in close proximity with a bent, bridging ligand. We demonstrate that ligand modification can be used to control the position of metalation into the different cavities (N\(_2\)O\(_2\) or O\(_2\)O\(_2\)) of such Schiff base ligands. This may be important for the realization of bimetallic systems for other applications. Electrochemical studies of L\(_4\), 4 and 6
demonstrate that the presence of Mn(II) influences the rate of ground-state charge transfer processes in such molecules.

5.3 Experimental

5.3.1 General procedures.

All chemicals were purchased from VWR International, Sigma Aldrich, Alfa Aesar or TCI America and used without further purification. Absorption spectra were recorded on an Olis RSM-1000 spectrometer using 1 cm Teflon-sealed quartz cuvettes. Attenuated total reflectance (ATR)-FTIR spectra were recorded with a Bruker Alpha ATR-FTIR. Magnetic susceptibilities were measured on a Quantum Design MPMS-XL7 SQUID Magnetometer. A saturation plot was measured at 2 K with the applied field being varied from 0~70000 oe. Temperature-dependent magnetic susceptibilities were performed from 2-300 K. Crystalline samples (ca. 10-30 mg) were loaded into gelcap/straw sample holders and mounted to the sample rod with Kapton tape for temperature dependence measurements. Multiple measurements were performed. The fitting results (such as g-factor, θ and J) from these separate data sets are consistent. The reported errors are based on several separate fitting results from different data sets. Electrochemical measurements were acquired on a BioLogic SP-200 potentiostat/galvanostat using a glassy carbon as working electrode, Ag/Ag⁺ reference electrode, and Pt wire counter electrode. Cyclic voltammetry was performed in a N₂ atmosphere glovebox in dimethyl sulfoxide solution and referenced to Fc/Fc⁺ = 0 V, with 0.1 M tetra-n-butylammonium hexafluorophosphate (TBAHFP) electrolyte. The scan rate was 200 mV/s unless otherwise noted. The ligands studied in this report are represented by the following abbreviations: H₄(fsa)₂en (L₁), N, N’-bis(3-carboxy-salicylidene)-1,2-diaminoethane; H₄(fmsa)₂en (L₂), N, N’-bis(3-carboxy-5-methyl-salicylidene)-1,2-
diaminoethane; H$_4$(fsa)$_2$tm (L$_3$), N, N’-bis(3-carboxy-salicylidene)-2,3-dimethyl-2,3-butanediylidiamine and H$_4$(fmsa)$_2$tm (L$_4$), N, N’-bis(3-carboxy-5-methyl-salicylidene)-2,3-dimethyl-2,3-butanediylidiamine.\textsuperscript{29-31}

5.3.2 X-Ray crystallography

Crystals were mounted on MiTeGen mounts and cooled to 100 K. X-ray intensity data were measured on a Bruker-Nonius X8 Kappa APEX II system equipped with a graphite monochromator and a MoK$_\alpha$ fine-focus sealed tube (\(\lambda = 0.71073\) Å). Unit cell dimensions were determined from symmetry constrained fits of the reflections. Frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the multi-scan method (SADABS). Structures were solved using direct methods (Bruker XS) and refined using the Bruker SHELX 2013\textsuperscript{32} software package using full-matrix least-squares refinement on F. All non-hydrogen atoms were identified in the original solution, or located from the difference map from refinement results. Hydrogen atoms were placed at idealized positions and allowed to ride on the nearest non-H atom. The figures of the molecular structures were created using Olex\textsuperscript{2} Crystallographic information files for all structures are available in the ESI\textsuperscript{†} and from the Cambridge Crystallographic Data Center (www.ccdc.cam.ac.uk). CCDC reference number: 3 (1453973), 6 (1453974)

5.3.3 Preparation of L$_1$-L$_4$

3-formylsalicylic acid and 3-formyl-2-hydroxy-5-methylbenzoic acid were synthesized using Duff’s approach.\textsuperscript{33} The 3-COOH substituted Schiff bases (L$_1$-L$_4$) were prepared by refluxing one equivalent of diamine and two equivalents of 3-formylsalicylic acid or 3-formyl-2-hydroxy-5-methylbenzoic acid in ethanol.\textsuperscript{34} L$_1$,\textsuperscript{29} L$_2$,\textsuperscript{31} and L$_3$\textsuperscript{30,31} have been previously reported. The characteristic spectra of L$_1$-L$_3$ are consistent with the literature. L$_4$ is prepared
in a similar fashion, using methanol as the solvent. (yellow powders, 0.17 g, 73.2%) ATR-FTIR (cm\(^{-1}\)): \(\nu_{\text{C=O}}\) 1702(s), \(\nu_{\text{C=N}}\) 1627(s). \(^1\)H-NMR ([D\(_6\)]dmsol, ppm.): 8.85 (2H, br, s, N=C(7)H), 7.90 (2H, br, s, C(6)H), 7.75 (2H, br, s, C(4)H), 2.26 (6H, s, C(10)H\(_3\)), 1.47, (12H, s, C(9)H\(_3\)). The OH and COOH protons are not observed.

Scheme 5.1. Schematic representation and carbon atom labelling for L\(_1\)-L\(_4\).

5.3.4 General procedure of vanadium(IV) ion complexation.

Mononuclear oxovanadium complexes 1-4, derived from L\(_1\)-L\(_4\), are prepared according to previously known approaches\(^{35}\) with slight modification. The procedure with L\(_4\) is selected as an example: in a 100 ml round bottom flask, 0.1 g (0.23 mmol) L\(_4\) was stirred as a suspension into a refluxing solution of 30 ml methanol and 3 ml pyridine. With the addition of 0.05 g (0.3 mmol) vanadium(IV) oxide sulfate hydrate, the yellow suspension turned green in approximately 10 mins. The mixture is further refluxed for 1.5 hour to allow completion. Desired compound 4 is separated as solid via vacuum filtration and washed with methanol.

\(\text{H}_2\text{VO(fsa)}_2\text{en}, (1)\).
1 is separated as orange red solid with yield of 0.084 g, 76.2%. ATR-FTIR (cm\(^{-1}\)): \(\nu_{\text{C}=\text{O}}\) 1733(s), \(\nu_{\text{C}=\text{N}}\) 1630(s), \(\nu_{\text{V}=\text{O}}\) 889(s). Anal. calc’d for C\(_{18}\)H\(_{14}\)N\(_2\)O\(_7\)V\(\cdot\)H\(_2\)O, C, 49.22; H, 3.67; N, 6.38. Found: C, 49.52; H, 3.69; N, 6.77. HRMS-ESI (M+H\(^{+}\)) calc’d for C\(_{18}\)H\(_{15}\)N\(_2\)O\(_7\)V: 422.0313. Found 422.0306.

\(\text{H}_2\text{VO(fmsa)}_{2}\text{en}, (2).\)

2 is separated as orange red solid with yield of 0.100 g, 85.1%. ATR-FTIR (cm\(^{-1}\)): \(\nu_{\text{C}=\text{O}}\) 1735(s), \(\nu_{\text{C}=\text{N}}\) 1630(s), \(\nu_{\text{V}=\text{O}}\) 889(s). Anal. calc’d for C\(_{20}\)H\(_{18}\)N\(_2\)O\(_7\)V, C, 53.46; H, 4.04; N, 6.23. Found: C, 53.24; H, 3.62; N, 6.74. HRMS-ESI (M+H\(^{+}\)) calc’d for C\(_{22}\)H\(_{23}\)N\(_2\)O\(_7\)V: 450.0626. Found 450.0613.

\(\text{H}_2\text{VO(fsa)}_{2}\text{tmen}, (3).\)

3 is separated as green solid with yield of 0.105 g, 90.8%. X-ray quality crystals were obtained via vapor diffusion of diethyl ether into a solution of methanol at room temperature. ATR-FTIR (cm\(^{-1}\)): \(\nu_{\text{C}=\text{N}}\) 1627(s), \(\nu_{\text{C}=\text{O}}\) 1607(s), \(\nu_{\text{V}=\text{O}}\) 977(s). Anal. calc’d for C\(_{22}\)H\(_{22}\)N\(_2\)O\(_7\)V, C, 55.35; H, 4.65; N, 5.87. Found: C, 56.89; H, 4.44; N, 5.42. HRMS-ESI (M+H\(^{+}\)) calc’d for C\(_{22}\)H\(_{23}\)N\(_2\)O\(_7\)V: 478.0939. Found 478.0937

\(\text{H}_2\text{VO(fmsa)}_{2}\text{tmen}, (4).\)

4 is separated as green solid with yield of 0.100 g, 87.4%. ATR-FTIR (cm\(^{-1}\)): \(\nu_{\text{C}=\text{N}}\) 1635(s), \(\nu_{\text{C}=\text{O}}\) 1582 (s), \(\nu_{\text{V}=\text{O}}\) 977(s). Anal. calc’d for C\(_{24}\)H\(_{26}\)N\(_2\)O\(_7\)V, C, 57.03; H, 5.19; N, 5.54. Found: C, 57.08; H, 5.19; N, 5.45. HRMS-ESI (M+H\(^{+}\)) calc’d for C\(_{24}\)H\(_{27}\)N\(_2\)O\(_7\)V: 506.1252, Found 506.1249;

5.3.5 Complexation of manganese(II) ion.

MnVO(fmsa)\(_2\)en, (5).
In a 20 ml vial, 0.030 g (0.067 mmol) 2 was stirred in 5 ml methanol. To this orange-red suspension, 5.6 mg (0.13 mmol) LiOH•H₂O was added and a dark green solution was formed. After that, a 1 ml aqueous solution of 13.2 mg (0.067 mmol) MnCl₂•4H₂O was added dropwise. The dark green solution turned to pale green, forming a white-green precipitate immediately after adding the MnCl₂ solution. The polymeric product was separated by vacuum filtration and washed with water and methanol. Yield: 12.2 mg, 37.3 %. ATR-FTIR (cm⁻¹): νC=N 1617(s), νC=O 1591(s), νV═O: 990(s). Anal. calc’d for C₂₀H₁₆MnN₂O₇V•H₂O, C, 46.17; H, 3.49; N, 5.38. Found: C, 46.18; H, 3.48; N, 5.52. HRMS-ESI (M+H⁺) calc’d for C₄₀H₃₄Mn₂N₄O₁₄V₂: 502.9850. Found 502.9845; (M+2H⁺) calc’d for C₆₀H₅₀Mn₃N₆O₂₁V₃: 753.9739. Found 753.9733; (M₃+Mn²⁺) calc’d for C₆₀H₄₈Mn₃N₆O₂₁V₃: 780.4351. Found 780.4340

MnVO(fmsa)₂tmen, (6)

A similar approach to 5 is used: in a 20 ml vial, 0.051 g (0.1 mmol) 4 was stirred in 5 ml methanol. To this green suspension, 8.4 mg (0.2 mmol) LiOH•H₂O was added and a blue-green solution was formed. After that, a 1 ml aqueous solution of 19.6 mg (0.1 mmol) MnCl₂•4H₂O was added dropwise. The blue-green solution turned to bright green over a period of 5 mins. Continuous adding MnCl₂ solution resulted in formation of a grass green precipitate, which was further separated by vacuum filtration. Yield: 36.8 mg, 58.2 %. X-ray quality crystals were obtained via vapor diffusion of diethyl ether into a solution of dimethyl sulfoxide at room temperature under the protection of N₂. UV/Vis (CH₂Cl₂) λₘₐₓ (nm)(ε (M⁻¹cm⁻¹)): (8200), 409 (970). ATR-FTIR (cm⁻¹): νC=O 1621(s), νV═O: 983(s). Anal. calc’d for C₂₄H₂₄MnN₂O₇V•(H₂O)₄(CH₃OH)₂, C, 47.94; H, 5.15; N, 4.47. Found: C, 48.41; H, 5.22; N, 4.61. HRMS-ESI (M+H⁺) calc’d for C₂₄H₂₅MnN₂O₇V•(CH₃)₂SO: 637.0616. Found 637.0609; calc’d for C₂₄H₂₅MnN₂O₇V•2(CH₃)₂SO: 715.0755. Found 715.0768.
5.4 Result and discussion

5.4.1 Synthesis and characterization

Scheme 5.2. Synthesis of bimetallic V(IV)-Mn(II) species 5 and 6. This is achieved by first making mononuclear V(IV) precursors 1-4 using Schiff bases L₁-L₄. The V(IV) ion binds to N₂O₂ sites when R₁ = H in 1 and 2, but binds to O₂O₂ sites when R₁ = CH₃ (3 and 4). Corresponding heterobimetallic V(IV)-Mn(II) complexes 5 and 6 are synthesized from 2 and 4 respectively. 5 is the repeat unit of the polymeric structure shown in Figure 5.S10. 6 has seven coordinate Mn(II) and shows L = DMSO after recrystallization from DMSO/diethyl ether. (Yield of 6: 58.2%)

The 3-carboxylic acid substituted Schiff bases (L₁-L₄) are prepared from a standard method by refluxing 1 equivalent of the diamine with 2 equivalents of the corresponding phenyl aldehyde in ethanol. In order to study the influence of ethylene backbone substitution on the metalation reactions, Schiff bases derived from 1,2-ethylenediamine and 1,1,2,2-tetramethyl-
1,2-ethylendiamine are compared. Mononuclear V(IV) complexes 1-4 (Scheme 5.2) are prepared by reacting 1 equivalent of VOSO$_4$ with the corresponding ligand in a refluxing pyridine-methanol (1:10, v/v) solution. Addition of Mn(II) produced the bimetallic products 5 and 6. This is achieved by the stepwise reaction of 2 and 4 with 2 equivalents of LiOH followed by 1 equivalent of MnCl$_2$ in methanol (Scheme 5.2). The composition of 1-6 is confirmed by elemental analysis and HR-ESI-MS. Structural information such as the coordination position is further studied by ATR-FTIR (Figure 5.3-S8) and X-ray crystallography (Figure 5.2).

Metalation of L$_1$-L$_4$ results in selective vanadium binding at either the N$_2$O$_2$ or the O$_2$O$_2$ site depending on the steric bulk of the ligand. Under the experimental conditions, V(IV) metalation of L$_1$ and L$_2$ yields products with V(IV) occupying the inner cavity (N$_2$O$_2$ site). In contrast, V(IV) metalation of L$_3$ and L$_4$ results in V(IV) occupying the outer cavity (O$_2$O$_2$ site). ATR-FTIR spectra of the carbonyl stretching frequencies for the 3-carboxylate/carboxylic acid groups for 1-4 confirm these assignments. As can be seen in Figure 5.1, for 1 and 2 the $\nu$C=O appears at 1733 cm$^{-1}$ and 1735 cm$^{-1}$, which is typical of non-coordinated carboxylic acid groups and indicates that the outer cavity is not occupied. However, $\nu$C=O for 3 and 4 are observed at 1607 cm$^{-1}$ and 1582 cm$^{-1}$ respectively, suggesting that V(IV) is in the outer O$_2$O$_2$ site. This is confirmed by X-ray crystallography of 3 as shown in Figure 5.2A. In 3, V(IV) coordinates into the outer O$_2$O$_2$ site and assumes a square pyramidal geometry with a V=O bond length of 1.60 Å. The ability of V(IV) to bind in either the inner N$_2$O$_2$ cavity or the outer O$_2$O$_2$ cavity is controlled by the backbone substituents, presumably due to the additional steric bulk of the backbone methyl groups in 3 and 4. Interestingly, Uemura et al$^{35}$ have reported a structural isomer of 3, showing coordination of V(IV) into the inner N$_2$O$_2$ site. We believe that they have observed a kinetic product, and under our conditions (refluxing methanol) we produce the
thermodynamic product with V(IV) in the O₂O₂ site. From this report and our results, it appears that both the N₂O₂ and O₂O₂ sites are accessible, however careful control of conditions is necessary to produce the desired product.

Figure 5.1 ATR-FTIR spectra of 1-4. The ν₃C=O at ~ 1733 cm⁻¹ and ν₅C=O at ~ 899 cm⁻¹ of 1 and 2 indicate non-coordinated carboxylic acid groups with V(IV) binding to the N₂O₂ site. The ν₃C=O at ~ 1600 cm⁻¹ and ν₅C=O at ~ 977 cm⁻¹ of 3 and 4 indicate the coordinated carboxylate groups with V(IV) binding to the O₂O₂ site.

The intermolecular V=O→V=O stacking of oxovanadium seems to be an additional factor that influences the molecular structure for 1-4. We conclude this based on differences of their ν₅V═O frequencies and colors (1 and 2 are red but 3 and 4 are green). As seen in Figure 5.1, due to the metalation in different locations, the ν₅V═O is found at 899 cm⁻¹ for 1 and 2 but is instead found at 977 cm⁻¹ for 3 and 4. We propose that the differences in ν₅V═O between 1-2 and 3-4 suggest that V=O→V=O stacking exists in 1-2 but is absent in 3-4. It has been suggested that
a weaker backbone steric hindrance when binding at N₂O₂ should facilitate such stacking.³⁷

The shifting of $\nu_{\text{V=O}}$ from 977 cm⁻¹ to 899 cm⁻¹ is also consistent with a change from monomeric five coordinate V(IV) to a polymeric six coordinate V=O→V=O chain. A similar red shift of $\nu_{\text{V=O}}$ also occurs when V=O coordinates to Lewis acids.³⁸ Consistent with previous reports of such structures, we observe that polymeric oxovanadium(IV) 1 and 2 are red, while monomeric 3 and 4 are green.³⁷ Increasing the reaction temperatures for 1 and 2 do not alter the position of V(IV) metalation.

![Figure 5.2 X-ray crystal structures of mononuclear V(IV) complex 3 (V=O = 1.5953 Å) and heterometallic Mn(II)-V(IV) complex 6 (V=O = 1.5999 Å; Mn−V = 3.2415 Å; Mn−O−V = 102.3°). Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms and non-bonded solvent molecules are omitted for clarity.](image)

Subsequent metalation of Mn(II) to 2 and 4 yields the Mn(II)-V(IV) heterometallic species 5 and 6 with yields of 37.3 % and 58.2%, respectively. The structure of the Mn(II)-V(IV) heterometallic complex 6 is shown in Figure 5.2B, confirming that the Mn(II) binds into the N₂O₂ cavity. The Mn(II) is found to have large out of plane displacement of ~1.2 Å relative to the N₂O₂ plane. Three DMSO solvent molecules are found to bind to the Mn(II) center,
resulting in unusual seven coordinate Mn(II) center with an unprecedented tetragonal base–
trigonal base (or 4:3) coordination geometry. To the best of our knowledge, only a singular
previous example of a 3d transition metal [(cyclen)V(CN)₃] has been reported with such a
geometry.⁴⁹ The distance between Mn and V is 3.24 Å and the Mn–O–V angle is 102°,
suggesting a weak metal-metal bond may exist between Mn and V. Crystallographic details of
⁴ and ⁶ are summarized in Table 5.S1.

Unlike ⁶, all attempts to crystalize ⁵ have been unsuccessful. However, disappearance of
νC=O at 1735 cm⁻¹ confirms coordination of Mn(II) into the O₂O₂ site and νV=O at 990 cm⁻¹
confirms five coordinate V(IV). Elemental analysis further confirms the proposed formula with
a 1:1 stoichiometry of Mn and V. However, HR-ESI-MS analysis reveals that ⁵ most likely
exists in a polymeric structure, since the precursor peak with the most abundant intensity is
found to be double charged (z = 2) with m/z = 780.4337. This m/z is consistent with a formula
of [M₃+Mn²⁺], where M is the repeated unit of the polymer with a formula C₂₀H₁₆MnN₂O₇V
(Scheme 5.2). Other signals such as m/z = 753.9733 (z = 2) and m/z = 502.9845 (z = 2)
represent fragments with compositions of [M₃+2H⁺] and [M₂+2H⁺]. Detailed mass spectra and
simulations are in SI (Figure 5.S11-12). A proposed polymeric structure is shown in Figure
5.S10, which is in agreement with the elemental analysis result of a 1:1 Mn-V stoichiometry
while also being able to generate the fragments observed by mass spectroscopy. In this
proposed structure, the Mn(II) is shared as bridging atom forming an alternating poly-
molecular chain with the salen ligand via binding between two O₂O₂ cavities (Figure 5.S10).
This is consistent with the relatively large atomic size of Mn(II) when compared to the O₂O₂
pocket, and is able to generate the z = 2 signals in HR-ESI-MS by the loss of one ligand. This
species may have a similar eight coordinate Mn(II) geometry as observed in a previous report.⁴⁰
5.4.2 Magnetic properties

In order to understand the magnetic exchange interaction between Mn(II) and V(IV) in this geometr, temperature-dependent magnetic susceptibility and variable-field magnetization were measured. As can be seen in Figure 5.3A (red), the product of $\chi T$ decreases with the decrease of temperature from 4.2 to 2.7 emu*K/mol illustrating antiferromagnetic coupling between Mn(II) and V(IV) in 6.

**Figure 5.3** Comparison of magnetic behavior of d$^1$-d$^5$ bimetallic Mn(II)-V(IV) under different conditions. (A). Temperature-dependent magnetic susceptibility for 6 (red) and a previously reported oxido bridge heterometallic Mn−O−V (blue). The fit is based on exchange spin Hamiltonian: $H = -2J\hat{S}_V \cdot \hat{S}_{Mn}$. (B). Variable field magnetization of 6 and Mn−O−V at 2 K. The structure (in-set) and magnetic study of Mn−O−V have been previously reported.

The Heisenberg-Dirac-Van Vleck Hamiltonian expression derived from $H = -2J\hat{S}_V \cdot \hat{S}_{Mn}$ with anisotropic $g_V$ and $g_{Mn}$ (equation 1) is used to fit the data, where $N$ is Avogadro's number, $k_B$ is the Boltzmann constant, $T$ is the temperature, $\beta$ is the Bohr magneton, $g$ is the electron g-factor, $\theta$ is the Weiss constant, $C$ represents the total contribution of temperature-independent-paramagnetic susceptibility (TIP) and diamagnetic susceptibility and $J$ corresponds to the net magnetic interaction between the paramagnetic centers. The best fit, as computed according to
equation 1, results in $J = -4.9 \pm 0.1 \text{ cm}^{-1}$, $\theta = -0.18 \pm 0.01 \text{ K}$, $g_{\text{Mn}} = 1.96 \pm 0.01$, $g_v = 1.88 \pm 0.02$ and $C = -6.32 \pm 0.30 \times 10^{-4} \text{ emu/mol}$ with $R^2 = 0.9999$. The $J$ value for 6 is antiferromagnetic, in contrast to the ferromagnetic coupling observed in the only other oxido-bridged heterometallic compound with the same $d^1$-$d^5$ electronic configuration: MnPyMe$_2$VO(tmtaa) (Mn-O-V, $J = +37.3 \text{ cm}^{-1}$, blue in Figure 5.3A).

$$\chi_M = \frac{NB^2}{3k_B(T-\theta)} \left( 3g_S^2 + 84g_S^2 e^{\frac{6J}{k_BT}} \right) + C, \quad g_1 = \frac{7g_{\text{Mn}} - g_v}{6}, \quad g_2 = \frac{5g_{\text{Mn}} + g_v}{6}$$

(1)

$$\frac{M}{N\mu_B} = gS B_j(x) B_j(x) = \frac{2S+1}{2S} \coth\left( \frac{2S+1}{2S} g_S B S \right) \times \frac{H}{T} - \frac{1}{2S} \coth\left( \frac{1}{2S} g_S B S \right) \times \frac{H}{T}$$

(2)

Antiferromagnetic coupling in 6 is further confirmed by variable field magnetization as shown in Figure 5.3B, which is distinct from the result for Mn-O-V. The fit of the Brillouin function (equation 2) yields a spin value of $S = 2$. Altering the sign of magnetic coupling $J$ between the Mn(II) and V(IV) confirms an important magneto-structural relationship for early 3d transition metals, demonstrating that both ferro- or antiferromagnetic coupling can be obtained by modifying bridging geometries.

Weihe and Güdel$^{42}$ theoretically predicted such a transformation from ferromagnetic to antiferromagnetic coupling in heterometallic systems with electronic configurations of $d^1$-$d^x$ ($x = 2$-$5$). This transition was suggested to occur when the bridge geometry bends away from linear (see Figure 5.S27). This was rationalized according to Anderson’s kinetic exchange model (also known as the orthogonalized magnetic orbital model$^{27}$)$^{43-48}$ The qualitative equations describing the kinetic exchange coupling $J$ in oxido-bridged heterometallic systems can be derived based on the Goodenough-Kanamori rules and the work of Weihe and Güdel.
Due to their correlation to ligand field parameters, accurate structural-magneto relationships can be established for previously known or unknown systems. According to this model, kinetic exchange interactions are described by the virtual electron transfer between two metal centers (metal-to-metal charge transfer, MMCT). Such MMCT excited states may mix with the ground states and result in the stabilization of ground states. Numerical expressions can be derived according to the electronic configuration and molecular symmetry (Figure 5.4A). The previously known heterometallic Mn-O-V, with the electronic configuration $d^1-d^5$, can be expressed using equation 3 in Figure 5.4A, where the antiferromagnetic contribution (the $-\frac{2}{5}h_{\gamma\gamma}^\prime$ term) comes from the so-called half to half transfer (the electron is taken from a half-filled orbital and moved to an already half-filled orbital, see equations 5-8 in SI). In these molecules, this transition is related to the interaction between the two $d_{xy}$ orbitals on manganese and vanadium. The ferromagnetic contributions (the positive terms, such as $\frac{1}{5}h_{\gamma\gamma}^\prime I^\prime$) are from the so-called half to zero transfer, where the electron is taken from a half-filled orbital and is transferred to an empty orbital. The overall $J$ value is expressed as the sum of all contributions and the sign of $J$ is determined by the dominant term. When ferromagnetic terms are dominant, such as the examples shown previously in linear geometries, ferromagnetic coupling is observed. Theoretically, it is possible to create a negative $J$ by increasing the antiferromagnetic contribution for this $d^1-d^5$ system ($-\frac{2}{5}h_{\gamma\gamma}^\prime$), which can be achieved by enhancing $d_{xy}$-$d_{xy}$ orbital overlap. The bis(phenoxido) bridged heterometallic complex 6 is the first example confirming this hypothesis.
Figure 5.4 (A). The orthogonalized magnetic orbital description for Mn-O-V\(^{38,41}\) based on kinetic exchange in C\(_{4}\) symmetry.\(^{48}\) The d orbitals are labelled as \(\varepsilon, \zeta, \xi, \eta\) and \(\theta\) for \(x^2-y^2\), \(yz\), \(xy\), \(xz\) and \(z^2\), respectively. (B). The natural magnetic orbital description for \(6\) based on potential exchange in \(C_{2v}\) symmetry.\(^{27}\) The magnetic orbitals are labelled as \(a_1\) (xy) for the V(IV) centered orbital and \(a_1\) (xy), \(a_1\) (\(z^2\)), \(a_2\) (yz), \(b_1\) (\(x^2-y^2\)) and \(b_2\) (xz) for the Mn(II) centered orbitals.

An important assumption for the kinetic exchange model is that the potential exchange interaction is negligible. This appears to be true for previously reported oxido-bridged systems,\(^{41,51,52}\) but for molecules with different bridging geometries the potential exchange interaction, which contributes to ferromagnetic coupling, cannot be neglected.\(^{28}\) An alternative qualitative description for describing magnetic exchange coupling utilizes potential exchange interactions.\(^{6,14,16,22,25-28}\) Since the bis(phenoxido)-bridged \(6\) belongs this well-studied family, the antiferromagnetic coupling between Mn(II) and V(IV) can also be rationalized based on potential exchange interactions (equation 4 in Figure 4B). According to the natural magnetic orbitals of \(6\), antiferromagnetic contributions arise from the interaction between the \(d_{xy}\) orbitals of both Mn(II) and V(IV) which both have the same symmetry (\(a_1\)), while ferromagnetic
contributions originate from the interactions between an a\textsubscript{1} orbital on V(IV) with the orthogonal a’\textsubscript{1}, a\textsubscript{2}, b\textsubscript{1} and b\textsubscript{2} orbitals on Mn(II). It is known that in bimetallic systems supported by similar ligands as 6 that the contributions from antiferromagnetic $J_{a_1a_1}$ and ferromagnetic $J_{a_1h_1}$ are the dominant interactions.\textsuperscript{16} For instance, the ferromagnetic term $J_{a_1a_1}$ in a Cu(II)V(IV) system is 59 cm\textsuperscript{-1},\textsuperscript{28} while the antiferromagnetic term $J_{a_1h_1}$ is -30 $\sim$ -128 cm\textsuperscript{-1} in several V(IV)V(IV) systems.\textsuperscript{53,54} Using these values for $J_{a_1a_1}$ and $J_{a_1h_1}$ as a starting point, $J$ would therefore be in the range of -14 $\sim$ +6 cm\textsuperscript{-1} according to equation 4. This is in agreement with the observed magnitude of $J$ for 6, -4.9 cm\textsuperscript{-1}. This result also suggests that stronger antiferromagnetic coupling should be observed in heterometallic systems with lower d-electron counts d\textsuperscript{1}-d\textsuperscript{x}, ($x = 2\sim4$), since the ferromagnetic contribution from $J_{a_1h_1}$ is absent when the $x^2$-$y^2$ orbital is unoccupied (Figure 4).

According to such analysis, we can simply understand the sign change of $J$ between the Mn(II)-V(IV) centers in the differing geometries of Mn-O-V and 6. The strong ferromagnetic coupling of linear Mn-O-V is primarily determined by mixing the charge transfer excited states, which stabilizes the $S = 3$ state. In contrast, the observed antiferromagnetic coupling of 6 is the net result from combining a strong antiferromagnetic exchange interaction via a direct interaction between xy orbitals of the same symmetry and a strong ferromagnetic exchange interaction that arises from orthogonal xy (V(IV)) and $x^2$-$y^2$ (Mn(II))orbitals. Although these two approaches are based on different models (kinetic exchange vs potential exchange) whose differences have been extensively described,\textsuperscript{27} the ultimate question as of which one is a better treatment for describing magnetic interactions remains an open question.\textsuperscript{55,56} We believe that
carefully utilizing a combination of both techniques allows for more accurate determination of magneto-structural relationships for heterometallic complexes in different geometries.

5.4.3 Cyclic voltammetry

The redox properties of a typical ligand (L₄) and its corresponding metalated complexes 4 and 6 were studied using cyclic voltammetry in DMSO, and are depicted in Figure 5.S16 with selected redox potentials being summarized in Table 5.1. that LiOH does not deprotonate the phenol and carboxylic acid groups.

<p>| Table 5.1 Redox potentials for L₄, 4 and 6. Signals are referenced to Fc/Fc⁺ at 0 V. |
|---------------------------------|-----|-----------------|-------------|-------------|-------------|-----------------|</p>
<table>
<thead>
<tr>
<th>V(V/IV)</th>
<th>Mn(III/II)</th>
<th>L¹⁺/L⁰</th>
<th>L⁰/L¹⁻</th>
<th>L¹⁻/L²⁻</th>
<th>Mn(II/I)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L₄</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Eₚc = -1.50</td>
<td>Eᵢₛ = -1.82</td>
</tr>
<tr>
<td>4</td>
<td>Eₚµ = 0.12</td>
<td>-</td>
<td>Eₚc = -0.18</td>
<td>Eₚa = -1.60</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>Eᵢ₃ = 0.028</td>
<td>Eᵢₛ = -0.22</td>
<td>Eₚc = -0.59</td>
<td>-</td>
<td>Eᵢₛ = -1.99</td>
</tr>
</tbody>
</table>

a Determined in high scan rate. b Only observed in the second scan

As shown in Figure 5.S17, L₄ demonstrates an irreversible reductive event at Eₚc = -1.50 V and a reversible redox event with Eᵢₛ = -1.82 V (all potentials are reported vs Fc⁺/Fc). Addition of excess LiOH does not change the redox properties, which indicates Oxovanadium complex 4 shows two similar ligand based redox events at Eₚc of -1.60 V and Eᵢ₃ of -1.94 V respectively. In contrast to L₄, the irreversible reductive response at -1.60 V
results in an additional irreversible oxidative wave with an anodic potential of $E_{pa} = -0.10$ V (Figure 5.S22) in the second scan. This may suggest a ligand based chemical reaction following the initial reduction. In the area of $-1.0 \sim 0.5$ V, where $L_4$ is electrochemically silent, an oxidation wave ($E_{pa} = 0.12$ V) and a reduction wave ($E_{pc} = -0.18$) are observed. The oxidative response at 0.12 V is assigned to the oxidation of V(IV) to V(V), consistent with typical V(V/IV) couples.\(^{36,57,58}\) However, in contrast to previous oxovanadium salen species which have reversible V(V/IV) couples, the wave at 0.12 V is irreversible. Interestingly, the following irreversible reductive wave ($E_{pc} = -0.18$ V) appears to be associated with the V(V/IV) oxidation event (Figure 5.S20). It is possible that a quick charge transfer reaction occurs after the oxidation of V(IV), generating a different species that produces the following reductive response ($E_{pc} = -0.18$ V). Repetitive scanning did not alter this redox couple (Figure 5.S21), which suggests that these irreversible processes do not lead to overall decompositions of 4. We propose an intramolecular charge transfer reaction to explain this behavior (Scheme 5.2). The oxovanadium(V) complex $[V(V)L^0]^+$ is formed upon oxidation of V(IV) at $E_{pa} = 0.12$ V. However, the resulting $[V(V)L^0]^+$ may have a short lifetime and undergoes a ligand-to-metal charge transfer to form $[V(IV)L^{1+}]^+$. The oxidized product $[V(IV)L^{1+}]^+$ can then be irreversibly reduced at $E_{pc} = -0.18$ V to reform the initial oxovanadium(IV) complex V(IV)L$^0$. The ligand oxidized intermediate is presumably a phenoxy radical complex, since such phenoxy radicals are commonly observed in similar ligand environments upon oxidation.\(^{59-62}\) Interestingly, a variable scan rate study (Figure 5.S19) from 100 mV/s to 1600 mV/s shows no significant changes for these two processes, indicating that the rate of charge transfer must be faster than the scan rate with the $k_f >> 1$ s$^{-1}$. 

Scheme 5.2. A) Schematic illustration of sequentially irreversible couples of 4 at $E_{pa} = 0.12$ V and $E_{pc} = -0.18$ V. No changes were observed when varying the scan rate from 100 to 1600 mV/s. B) The irreversible couples of 6 at $E_{pa} = 0.10$ V and $E_{pc} = -0.59$ V. The cathodic response relating to $E_{pa} = 0.10$ V is shifted to $E_{pc} = -0.04$ V at faster scan rates.

Addition of Mn(II) resulted in significant differences between the cyclic voltammetry of 6 and 4. As can be seen in Figure 5.23 and Table 5.1, previously observed ligand based irreversible peaks at around $-1.50\sim1.60$ V for L4 and 4 are not present, but the reversible ligand based redox event at $E_{1/2} = -1.99$ V can still be observed. An additional irreversible reductive event is observed at $E_{pc} = -2.43$ V, which may be related to Mn(II/I). The new reversible redox couple observed at $E_{1/2} = -0.22$ is assigned to Mn(III/II) (Figure 5.S25). The previously observed irreversible redox couple is still present, with the irreversible anodic peak at $E_{pa} = 0.10$ V while the cathodic peak is at $E_{pc} = -0.59$ V. Although separated by almost 0.7 V, the cathodic peak remains associated with the anodic peak (Figure 5.S24) suggesting that the redox process is similar to that proposed for 4 (scheme 2B). However, a variable scan rate study indicates that the charge transfer rate is much slower in 6 than in 4. As shown in Figure 5.S26, the cathodic current at -0.59 V continuously disappears while a new cathodic current at -0.042 V appears at faster scan rates. We proposed that the charge transfer reaction rate ($k_f$) is therefore of similar magnitude to the scan rate with $k_f$ being $0.1 \sim 1$ s$^{-1}$. The significant $k_f$ differences and redox
potential change from -0.18 V to -0.59 V of the same chemical redox processes for 4 and 6 suggest the additional Mn(II) coordination in 6 alters both the redox potentials and the rate of intramolecular charge transfer process.

5.5 Conclusion

This experimental demonstration that geometry can be used to change the sign of exchange coupling (J) for a d\(^1\)-d\(^x\) (x = 2~5) system is potentially general. We propose that this model can be applied not only to understand exchange coupling in ground state molecules, but can also be used to design magnetic coupling in excited states of MMCT chromophores.\(^{51,63}\) It has been suggested that generating spin-trapped MMCT excited states is important for extending the excited state lifetime of such chromophores.\(^{51,63-65}\) Utilizing ground state models such as 6 enables the estimation of sign and magnitude for exchange coupling in MMCT excited states and can thus provide guidance for the rational design of MMCT chromophores with long-lived charge separated states. For instance, since antiferromagnetic coupling is anticipated for bent oxido-bridged geometries with d\(^1\)-d\(^x\) (x = 1~4), a spin-trapped state can only be obtained when the corresponding ground state of d\(^0\)-d\(^y\) (y = 2~5) is high spin. For a Mn(II)Ti(IV) chromophore,\(^{64}\) this results in a 5/2 ground state and a 3/2 MMCT excited state. In contrast, when a d\(^1\)-d\(^y\) (x = 1~4) complex is in a linear geometry ferromagnetic coupling is expected. Therefore, a spin-trapped state can only be obtained when the ground state is low-spin for d\(^0\)-d\(^y\) (y = 2~5), which for a Mn(II)Ti(IV) chromophore would result in a 3/2 ground state and a 5/2 MMCT excited state. Ultimately, determining if such a link exists between bridging geometries and excited state properties (such as lifetime) will allow for a better estimation of electronic and magnetic coupling in polymetallic species that undergo MMCT. This is enabled
through the determination of magnetic coupling in compounds with electronic configurations similar to those of MMCT excited states such as 6.\textsuperscript{41,51}

In summary, we have prepared and structurally characterized several 3-carboxylic acid substituted Schiff bases and studied their backbone influences on the complexation of V(IV) and Mn(II). The steric hindrance group is able to generate the complexation of V(IV) in the outer O\textsubscript{2}O\textsubscript{2} cavity while non-steric hindrance group show the binding in inner N\textsubscript{2}O\textsubscript{2} cavity. The electrochemical properties of these systems are further characterized by cyclic voltammetry. The influence of addition Mn(II) complexation is found to alter the potential and rate of the intramolecular charge transfer. The magnetic exchange coupling of heterometallic Mn(II)V(IV) in this bis(phenoxido) geometry is compared with the Mn-O-V in linear geometry, which reveals the bridging geometry is the essential factor to alter the sign of exchange coupling for such system. This is the first experimental demonstration for such early 3d transition metal couple.
5.6 Supporting information

X-ray Crystallography Detail

![X-ray Crystal Structure](image)

**Figure 5.S1.** X-ray crystal structure of 3. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms except the N-H bond and solvent molecules are omitted for clarity.

A clear light brown plate-like specimen of C$_{22}$H$_{22}$N$_2$O$_7$V, approximate dimensions 0.567 mm $\times$ 0.445 mm $\times$ 0.225 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

A total of 994 frames were collected. The total exposure time was 8.32 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 72056 reflections to a maximum $\theta$ angle of 33.727° (0.64 Å resolution), of which 9789 were independent (average redundancy 7.36, completeness = 99.9 %, $\text{R}_{\text{int}} = 3.72\%$, $\text{R}_{\text{sig}} = 2.07\%$) and 8305
(84.84%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 27.5418(7) \text{ Å}$, $b = 12.2049(3) \text{ Å}$, $c = 14.5894(4) \text{ Å}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, volume = 4904.2(2) \text{ Å}^3$, are based upon the refinement of the XYZ-centroids of 9778 reflections above 20 $\sigma(I)$ with $5.262^\circ < 2\theta < 68.942^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.8700.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group Pccn, with $Z = 8$ for the formula unit, C$_{22}$H$_{22}$N$_2$O$_7$V. The final anisotropic full-matrix least-squares refinement on $F_2$ with 301 variables converged at $R_1 = 5.05\%$, for the observed data and $wR_2 = 12.87\%$ for all data. The goodness-of-fit was 1.157. The largest peak in the final difference electron density synthesis was $0.501 \text{ e/Å}^3$ and the largest hole was $-0.598 \text{ e/Å}^3$ with an RMS deviation of 0.078 $\text{ e/Å}^3$. On the basis of the final model, the calculated density was 1.293 g/cm$^3$ and F(000), 1976.0 e$^-$. SQUEEZE of PLATON was applied to deal with disordered solvent. Analysis revealed 1126 cubic angstroms of void space and 348 electrons house therein. This approximates to 12 CH$_3$OH per unit cell, or 1.5 per formula unit.
**Figure 5.S2.** X-ray crystal structure of 6. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms and solvent molecules (except for coordinated) are omitted for clarity.

A clear light green plate-like specimen of C₆₀H₈₄Mn₂N₄O₂₀S₆V₂, approximate dimensions 0.514 mm × 0.371 mm × 0.084 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

A total of 2737 frames were collected. The total exposure time was 19.47 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 211781 reflections to a maximum θ angle of 28.402° (0.75 Å resolution), of which 17327 were independent (average redundancy 12.22, completeness = 99.9 %, Rint = 2.97%, Rsig = 1.34%) and 15536 (89.66%) were greater than 2σ(F²). The final cell constants of a = 11.1241(3) Å, b = 16.1706(5) Å, c = 20.3298(6) Å, α = 107.130(2)°, β = 96.888(2)°, γ = 90.948(2)°, volume = 3464.35(18) Å³, are
based upon the refinement of the XYZ-centroids of 9559 reflections above 20 $\sigma$(I) with $4.558^\circ < 2\theta < 74.068^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.7554.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P-1, with $Z = 2$ for the formula unit, $C_{60}H_{84}Mn_2N_4O_{20}S_6V_2$. The final anisotropic full-matrix least-squares refinement on $F^2$ with 891 variables converged at $R_1 = 3.42\%$, for the observed data and $wR_2 = 9.34\%$ for all data. The goodness-of-fit was 1.095. The largest peak in the final difference electron density synthesis was $1.478 \text{ e/Å}^3$ and the largest hole was $-0.709 \text{ e/Å}^3$ with an RMS deviation of $0.078 \text{ e/Å}^3$. On the basis of the final model, the calculated density was $1.520 \text{ g/cm}^3$ and $F(000), 1648.0 \text{ e}^\cdot$. 
<table>
<thead>
<tr>
<th>Identification</th>
<th>3</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCDC number</td>
<td>1453973</td>
<td>1453974</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C_{22}H_{22}N_{2}O_{7}V</td>
<td>C_{60}H_{84}Mn_{2}N_{4}O_{20}S_{6}V_{2}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>477.35</td>
<td>1585.43</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>99.86</td>
<td>100.0</td>
</tr>
<tr>
<td>Crystal system</td>
<td>orthorhombic</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>Pccn</td>
<td>P-1</td>
</tr>
<tr>
<td>a/Å</td>
<td>27.5418(7)</td>
<td>11.1241(3)</td>
</tr>
<tr>
<td>b/Å</td>
<td>12.2049(3)</td>
<td>16.1706(5)</td>
</tr>
<tr>
<td>c/Å</td>
<td>14.5894(4)</td>
<td>20.3298(6)</td>
</tr>
<tr>
<td>α/°</td>
<td>90</td>
<td>107.130(2)</td>
</tr>
<tr>
<td>β/°</td>
<td>90</td>
<td>96.888(2)</td>
</tr>
<tr>
<td>γ/°</td>
<td>90</td>
<td>90.948(2)</td>
</tr>
<tr>
<td>Volume/Å³</td>
<td>4904.2(2)</td>
<td>3464.35(18)</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
<td>2</td>
</tr>
<tr>
<td>ρ_{calc}/g/cm³</td>
<td>1.293</td>
<td>1.520</td>
</tr>
<tr>
<td>μ/mm⁻¹</td>
<td>0.446</td>
<td>0.872</td>
</tr>
<tr>
<td>F(000)</td>
<td>1976.0</td>
<td>1648.0</td>
</tr>
<tr>
<td>Crystal size/mm³</td>
<td>0.567 × 0.445 × 0.225</td>
<td>0.514 × 0.371 × 0.084</td>
</tr>
<tr>
<td>Radiation</td>
<td>MoKα (λ = 0.71073)</td>
<td>MoKα (λ = 0.71073)</td>
</tr>
<tr>
<td>2Θ range for data collection/°</td>
<td>4.596 to 67.454</td>
<td>2.64 to 56.804</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-42 ≤ h ≤ 43, -19 ≤ k ≤ 19, -22 ≤ l ≤ 1</td>
<td>-14 ≤ h ≤ 14, -21 ≤ k ≤ 21, -27 ≤ l</td>
</tr>
<tr>
<td></td>
<td>≤ 12</td>
<td>≤ 27</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>72056</td>
<td>211781</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>9789 [R_{int} = 0.0382, R_{sigma} = 0.0207]</td>
<td>17327 [R_{int} = 0.0297, R_{sigma} = 0.0134]</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>9789/0/301</td>
<td>17327/6/891</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.157</td>
<td>1.095</td>
</tr>
<tr>
<td>Final R indexes [I&gt;=2σ (I)]</td>
<td>R₁ = 0.0505, wR₂ = 0.1226</td>
<td>R₁ = 0.0342, wR₂ = 0.0885</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>R₁ = 0.0612, wR₂ = 0.1287</td>
<td>R₁ = 0.0402, wR₂ = 0.0934</td>
</tr>
<tr>
<td>Largest diff. peak/hole / e Å⁻³</td>
<td>0.50/-0.60</td>
<td>1.48/-0.71</td>
</tr>
</tbody>
</table>
Solid state ATR-FTIR of 1-6 and electronic absorption spectra of 6

Figure 5.S3. Solid state ATR-FTIR spectrum of 1.

Figure 5.S4. Solid state ATR-FTIR spectrum of 2. (Check 2600, 3500-500)
Figure 5.S5. Solid state ATR-FTIR spectrum of 3.

Figure 5.S6. Solid state ATR-FTIR spectrum of 4.
Figure 5.S7. Solid state ATR-FTIR spectrum of 5.

Figure 5.S8. Solid state ATR-FTIR spectrum of 6. (DMSO)
Figure 5.S9. Molar absorptivity (in dimethyl sulfoxide) spectrum of 6.

HRMS-ESI results of 5 and 6 including simulated patterns.

Figure 5.S10. HR-ESI-MS spectrum of 5 in the range of m/z = 200 ~ 1000. A schematic structure for the corresponding precursor peak is shown on the right.
Figure 5.S11. A) Observed [M$_3$+2H$^+$] fragment of 5. B) Simulation pattern for the observed [M$_3$+2H$^+$] fragment of 5.

Figure 5.S12. A) Observed [M$_3$+Mn$^{2+}$] fragment of 5. B) Simulation pattern for the observed [M$_3$+Mn$^{2+}$] fragment of 5.
Figure 5.S13. A) Observed [M+DMSO+H\(^+\)] fragment of 6. B) Simulation pattern for the observed [M+DMSO+H\(^+\)] fragment of 6.

Figure 5.S14. A) Observed [M+2DMSO+H\(^+\)] fragment of 6. B) Simulation pattern for the observed [M+2DMSO+H\(^+\)] fragment of 6.
Details for the empirical computation of $J$ for linear Mn-O-V system\textsuperscript{41,42}

**Table 5.S2. Expressions for the kinetic exchange interaction of $J$**

<table>
<thead>
<tr>
<th>Interaction Type\textsuperscript{a}</th>
<th>Expression\textsuperscript{b,c}</th>
<th>Label</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\frac{1}{2}]_A \rightarrow [\frac{1}{2}]_B$</td>
<td>$-\frac{1}{n_A n_B} \frac{h_{ij}^2}{U}$</td>
<td>(5)</td>
</tr>
<tr>
<td>$[\frac{1}{2}]_A \rightarrow [0]_B$</td>
<td>$+ \frac{1}{n_A} \frac{h_{ij}^2 I}{U U}$</td>
<td>(6)</td>
</tr>
<tr>
<td>$[1]_A \rightarrow [\frac{1}{2}]_B$</td>
<td>$+ \frac{1}{n_B} \frac{h_{ij}^2 I}{U U}$</td>
<td>(7)</td>
</tr>
<tr>
<td>$[1]_A \rightarrow [0]_B$</td>
<td>$-\frac{(n_A - n_B)}{(n_A + 1)(n_B + 1)} \frac{h_{ij}^2 I}{U U}$</td>
<td>(8)</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Interaction type represents the virtual electron transfer from site A to site B. For example, the half to half transfer ($[\frac{1}{2}]_A \rightarrow [\frac{1}{2}]_B$) represents the process where you transfer one electron from A to an orbital on B, which then pair up in the orbital on B. This electron transfer process would result the formation of a low spin excited state, which is represented by a negative sign in these expressions.

\textsuperscript{b} The original expressions are based on $\hat{H}_{ab} = +J_{ab}\hat{S}_a\hat{S}_b$, while we use $\hat{H}_{ab} = -2J_{ab}\hat{S}_a\hat{S}_b$. The “-2” fold difference is applied in the final expressions.

\textsuperscript{c} $n_A$ and $n_B$ stand for the number of unpaired electrons, $h_{ij}$ is the transfer integral (see equation 9-14 in Figure 5.S15 for detail), $U$ is the energy required for this electron transfer to occur.
\begin{align}
  h_{\zeta\zeta} &= \langle \zeta_a | \hat{V}_{AB} | \zeta_b \rangle = \langle \zeta_b | \hat{V}_{AB} | \zeta_a \rangle \quad (9) \\
  h_{\eta\eta} &= \langle \eta_a | \hat{V}_{AB} | \eta_b \rangle = \langle \eta_b | \hat{V}_{AB} | \eta_a \rangle \quad (10) \\
  h_{\xi\xi} &= \langle \xi_a | \hat{V}_{AB} | \xi_b \rangle = \langle \xi_b | \hat{V}_{AB} | \xi_a \rangle \quad (11) \\
  h_{\varepsilon\varepsilon} &= \langle \varepsilon_a | \hat{V}_{AB} | \varepsilon_b \rangle = \langle \varepsilon_b | \hat{V}_{AB} | \varepsilon_a \rangle \quad (12) \\
  h_{\theta\theta} &= \langle \theta_a | \hat{V}_{AB} | \theta_b \rangle = \langle \theta_b | \hat{V}_{AB} | \theta_a \rangle \quad (13) \\
  h_{\eta\theta} &= \langle \eta_a | \hat{V}_{AB} | \eta_b \rangle = \langle \eta_b | \hat{V}_{AB} | \eta_a \rangle = \langle \theta_a | \hat{V}_{AB} | \theta_b \rangle = \langle \theta_b | \hat{V}_{AB} | \theta_a \rangle \quad (14)
\end{align}

Figure 5.S.15. Schematic illustration of important one-electron transfer integrals. The transfer integrals $h_{\zeta\zeta}$, $h_{\eta\eta}$, $h_{\xi\xi}$, $h_{\varepsilon\varepsilon}$, $h_{\theta\theta}$ and $h_{\eta\theta}$ are shown using double arrows.

Table 5.S.2. Theoretical $J$ values for electronic configurations of linear Mn-O-V$^{41,42}$

<table>
<thead>
<tr>
<th>m,n</th>
<th>d$^m$</th>
<th>d$^a$</th>
<th>$J_{calc}^{a,b}$</th>
<th>Label</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,5</td>
<td>$\zeta$</td>
<td>$\zeta$</td>
<td>$\eta\xi\theta\varepsilon$</td>
<td>$-\frac{2}{5} h_{\zeta\zeta} + \frac{1}{5} h_{\eta\eta} I + \frac{1}{5} h_{\xi\xi} I + \frac{1}{5} h_{\varepsilon\varepsilon} I' + \frac{1}{5} h_{\eta\theta} I + \frac{1}{5} h_{\theta\theta} I' + \frac{1}{5} h_{\xi\xi} I'$</td>
</tr>
</tbody>
</table>

$^a$ due to $U$ being unknown, the effective parameters $\frac{h_{ij}}{U} = h_{ij}'$ and $\frac{I}{U} = I'$ are used

$^b$ expressions are derived from the one-electron transfer integrals: equation 5-8.
Table 5.S3. Angular-dependent ligand field parameters used in the transfer integrals.\textsuperscript{42,45}

<table>
<thead>
<tr>
<th>Equations</th>
<th>Label</th>
</tr>
</thead>
<tbody>
<tr>
<td>$h_{n\theta}(\phi) = \sqrt{e_\pi e_{cp}} \sin(\phi)$</td>
<td>(16)</td>
</tr>
<tr>
<td>$h_{\phi\theta}(\phi) = e_{\alpha} + e_{cp} \cos(\phi)$</td>
<td>(17)</td>
</tr>
<tr>
<td>$h_{\phi\eta}(\phi) = e_\pi (-\cos(\phi))$</td>
<td>(18)</td>
</tr>
<tr>
<td>$h_{\eta\eta}(\phi) = e_\pi$</td>
<td>(19)</td>
</tr>
<tr>
<td>$h_{xx}(\phi) = x(180 - \phi)$</td>
<td>(20)</td>
</tr>
</tbody>
</table>

Table 5.S4. Theoretical $J$ values based on angular-dependent ligand field parameters for linear Mn-O-V

<table>
<thead>
<tr>
<th>#</th>
<th>$J_{\text{calc}}$ \textsuperscript{a,b}</th>
<th>Label</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$-\frac{2}{5} x'^2 (180 - \phi)^2 + \frac{1}{5} e_\pi'^2 \cos^2(\phi) I' + \frac{1}{5} e_\sigma'^2 I' + \frac{1}{5} e_{cp}' \sin^2(\phi) I' + \frac{1}{5} (e_{\alpha}' + e_{cp}' \cos(\phi))^2 I'$</td>
<td>(21)</td>
</tr>
</tbody>
</table>

\textsuperscript{a} expression is based on equation 14-18 in Table 5.S3 and effective parameters: $\frac{e_\pi}{\sqrt{U}} = e_\pi'$,

$\frac{e_{cp}}{\sqrt{U}} = e_{cp}'$, $\frac{e_{\alpha}}{\sqrt{U}} = e_{\alpha}'$, $x = x'$, $\frac{I}{U} = I'$ are used.

\textsuperscript{b} A graphical presentation of these equations using the empirical effective parameters $x' = 0.19$ cm$^{-1/2}$; $I' = 0.29$; $e_\pi' = 20.86$ cm$^{-1/2}$; $e_{\alpha}' = 18.42$ cm$^{-1/2}$; $e_{cp}' = 39.46$ cm$^{-1/2}$ can be seen in (Figure 5.5) Weihe and Güdel’s previous work.\textsuperscript{42}
Electrochemical Details of L₄, 4 and 6

**Figure 5.S16.** Cyclic voltammetry of (L₄), 4 and 6 in degassed dimethyl sulfoxide (DMSO) with 0.1 M tetrabutylammonium hexafluorophosphate using glassy carbon working electrode, platinum counter electrode and silver wire quasi reference electrode with scan rate of 200 mv/s. All signals were referenced to ferrocene/ferrocenium (Fc/Fc⁺) at 0 V. The asterisk labelled peak represents the residue H₂O signal in DMSO. Ferrocene has been added L₄ measurement for comparison.
**Figure 5.S17.** Cyclic voltammetry of complex L₄ with 4 equivalents of LiOH in degassed dimethyl sulfoxide (DMSO) with 0.1 M tetrabutylammonium hexafluorophosphate using glassy carbon working electrode, platinum counter electrode and silver wire quasi reference electrode with Fc/Fc⁺ set at 0 V (scan rate: 200 mv/s). Ferrocene has been added L₄ measurement for comparison.

**Figure 5.S18.** Cyclic voltammetry of 4 in degassed dimethyl sulfoxide (DMSO) with 0.1 M tetrabutylammonium hexafluorophosphate using glassy carbon working electrode, platinum counter electrode and silver wire quasi reference electrode with Fc/Fc⁺ set at 0 V and scan rate of 200 mv/s. The proposed electrochemical processes are depicted. The asterisk labelled peak represents oxidation of the residual H₂O in DMSO.
Figure 5.S19. Cyclic voltammetry of 4 with variable scan rates in degassed dimethyl sulfoxide (DMSO) with 0.1 M tetrabutylammonium hexafluorophosphate using glassy carbon working electrode, platinum counter electrode and silver wire quasi reference electrode with Fc/Fc$^+$ set at 0 V. For better comparison, the currents are normalized to the square root of scan rate ($v^{1/2}$). The asterisk labelled peak represents oxidation of the residual H$_2$O in DMSO.

Figure 5.S20. Cyclic voltammetry of 4 with variable scanning voltage range in degassed dimethyl sulfoxide (DMSO) with 0.1 M tetrabutylammonium hexafluorophosphate using
glassy carbon working electrode, platinum counter electrode and silver wire quasi reference electrode with Fc/Fc⁺ set at 0 V and scan rate of 200 mv/s.

**Figure 5.S21.** Cyclic voltammetry of 4 with repetitive scanning in degassed dimethyl sulfoxide (DMSO) with 0.1 M tetrabutylammonium hexafluorophosphate using glassy carbon working electrode, platinum counter electrode and silver wire quasi reference electrode with Fc/Fc⁺ set at 0 V and scan rate of 200 mv/s.
**Figure 5.S22.** Cyclic voltammetry of 4 with variable scanning voltage range and repetitive scanning in degassed dimethyl sulfoxide (DMSO) with 0.1 M tetrabutylammonium hexafluorophosphate using glassy carbon working electrode, platinum counter electrode and silver wire quasi reference electrode with Fc/Fc$^+$ set at 0 V and scan rate of 200 mv/s.

**Figure 5.S23.** Cyclic voltammetry of 6 in degassed dimethyl sulfoxide (DMSO) with 0.1 M tetrabutylammonium hexafluorophosphate using glassy carbon working electrode, platinum counter electrode and silver wire quasi reference electrode with Fc/Fc$^+$ set at 0 V and scan rate of 200 mv/s.
counter electrode and silver wire quasi reference electrode with Fc/Fc⁺ set at 0 V and scan rate of 200 mv/s. The proposed electrochemical processes are depicted.

Figure 5.S24. Cyclic voltammetry of 6 with variable scanning voltage range in degassed dimethyl sulfoxide (DMSO) with 0.1 M tetrabutylammonium hexafluorophosphate using glassy carbon working electrode, platinum counter electrode and silver wire quasi reference electrode with Fc/Fc⁺ set at 0 V and scan rate of 200 mv/s.
**Figure 5.S25.** Cyclic voltammetry of 6 with repetitive scanning in degassed dimethyl sulfoxide (DMSO) with 0.1 M tetrabutylammonium hexafluorophosphate using glassy carbon working electrode, platinum counter electrode and silver wire quasi reference electrode with Fc/Fc$^+$ set at 0 V and scan rate of 200 mv/s.
Figure 5.S26. Cyclic voltammetry of 6 with variable scan rates in degassed dimethyl sulfoxide (DMSO) with 0.1 M tetrabutylammonium hexafluorophosphate using glassy carbon working electrode, platinum counter electrode and silver wire quasi reference electrode with Fc/Fc\(^+\) set at 0 V. For better comparison, the currents are normalized to the square root of scan rate (v\(^{1/2}\)).

![Graph of cyclic voltammetry](image)

Figure 5.S27. Schematic demonstration of ferro- to antiferromagnetic coupling change according to angular overlap model.\(^42\)

5.7 Acknowledgment

This work was supported by generous startup funding from North Carolina State University. We acknowledge Dr. Daniel Stasiw and Prof. David A. Shultz for assistance in collecting SQUID data. Mass spectra were obtained at the NCSU Department of Chemistry Mass Spectrometry Facility.

5.8 References


(34) Pfeiffer, P.; Breith, E.; Lübbe, E.; Tsumaki, T. Liebigs Ann. 1933, 503, 84.


(49) Schäffer, C. E. Struct. Bond. 1968, 5, 68.


CHAPTER 6

On the Origin of Ferromagnetic Coupling in μ-Oxido-Bridged Heterometallic Complexes

This manuscript was prepared to submit to Inorg. Chem.

T. Huang, X. Wu, W. W. Weare, R. D. Sommer

Huang, T performed all magnetization work and Wu, X. performed all the synthesis work.

Department of Chemistry, North Carolina State University;

Raleigh, NC, 27695-8204
6.1 Abstract

Modeling the exchange interaction of oxido-bridged heterometallic complexes are important to understand their metal-metal interactions. The magnetic exchange coupling for all of the structurally known mono-oxido-bridged heterobimetalliclic M←O═V^{IV} complexes, where M = Cr^{III} (1), Mn^{III} (2), Mn^{II} (3), Fe^{II} (4), Co^{II} (5), Ni^{II} (6) and Cu^{II} (7) are summarized. Ferromagnetic coupling is observed for all complexes except 4, with J values of +42.5 cm\(^{-1}\) (1), +2.6 cm\(^{-1}\) (2), +38 cm\(^{-1}\) (3), +39 cm\(^{-1}\) (5), +22.5 cm\(^{-1}\) (6), and +11.7 cm\(^{-1}\) (7), respectively (according to the spin-Hamiltonian \(H = -2J\mathbf{S}_1\cdot\mathbf{S}_2\)). Due to the presence of low spin d\(^6\) Fe^{II}, 4 shows no exchange interaction between V^{IV} and Fe^{II}. The observed ferromagnetic interactions are rationalized using a kinetic exchange model. A least squares fit using these experimental J values allows for the parameterization of the transfer integrals for the kinetic interactions that lead to ferromagnetic coupling across such mono-oxido-bridges. Empirical values for the transfer integrals based on \(\pi\) interactions (\(h'_{\pi\pi} I' = 58.5\) cm\(^{-1}\)) and a \(\sigma\) interaction (\(h'_{\sigma\sigma} I' = 88.1\) cm\(^{-1}\)) are obtained and used to model the magnitude of ferromagnetic coupling in these molecules. The presence of ferromagnetic coupling in 7 is rationalized by altering the ordering of its magnetic orbitals due to the Jahn-Teller distortion. This increases the \(\pi\)-\(\pi\) and \(\sigma\)-\(\sigma\) exchange interactions between V^{IV} and Cu^{II}, which otherwise should exhibit weak magnetic interaction. This model can therefore be used to identify unusual interactions across such oxido-bridges.

6.2 Introduction

Polynuclear metallic molecules are of significant interest and serve as models for studying and understanding fundamental theories for a wide-range of chemical processes. This includes natural-occurring\(^1\)\(^-\)\(^7\) or synthetic\(^8\)\(^-\)\(^12\) catalysts that utilize cooperativity, metal-metal charge
transfer (MMCT) chromophores for artificial photosynthesis\textsuperscript{13-24} and molecular level electronic device for data storage and quantum computing.\textsuperscript{25-35}

**Table 6.1** Expressions for the kinetic exchange interaction of $J$\textsuperscript{36}

<table>
<thead>
<tr>
<th>Interaction Type$^a$</th>
<th>Expression$^{b,c}$</th>
<th>Label</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\frac{1}{2}]_A \rightarrow [\frac{1}{2}]_B$</td>
<td>$- \frac{1}{n_An_B} \frac{h_{ij}^2}{U}$</td>
<td>(1)</td>
</tr>
<tr>
<td>$[\frac{1}{2}]_A \rightarrow [0]_B$</td>
<td>$+ \frac{1}{n_A} \frac{h_{ij}^2}{U} \frac{I}{U}$</td>
<td>(2)</td>
</tr>
<tr>
<td>$[1]_A \rightarrow [\frac{1}{2}]_B$</td>
<td>$+ \frac{1}{n_B} \frac{h_{ij}^2}{U} \frac{I}{U}$</td>
<td>(3)</td>
</tr>
<tr>
<td>$[1]_A \rightarrow [0]_B$</td>
<td>$- \frac{(n_A - n_B)}{(n_A + 1)(n_B + 1)} \frac{h_{ij}^2}{U} \frac{I}{U}$</td>
<td>(4)</td>
</tr>
</tbody>
</table>

$^a$ Interaction type represents the virtual electron transfer from site A to site B. See ref 65 for detail.

$^b$ The original expressions are based on $\hat{H}_{ab} = +J_{ab}\hat{S}_a\hat{S}_b$, while we use $\hat{H}_{ab} = -2J_{ab}\hat{S}_a\hat{S}_b$. The “-2” fold difference is applied in the final expressions.

$^c$ $n_A$ and $n_B$ stand for the number of unpaired electrons, $h_{ij}$ is the transfer integral, $U$ is the energy required for this electron transfer to occur, see Weihe and Güdel’s report\textsuperscript{36} for detail of parameters’ meaning.

Bimetallic complexes consisting of transition metal ions with unpaired spins play a significant role in elucidating the mechanisms of exchange interactions between such paramagnetic centers.\textsuperscript{37-55} Heisenberg,\textsuperscript{56} Dirac,\textsuperscript{57} and Van Vleck (HDVV)\textsuperscript{58} have shown that exchange coupling can be treated using an effective Hamiltonian, $H = -2JS_1S_2$, where the $J$ is known as the exchange coupling constant. According to Anderson’s model,\textsuperscript{59,60} $J$ involves both a potential and a kinetic exchange contribution and the total exchange coupling constant can be decomposed into a ferromagnetic term ($J_F > 0$) and an antiferromagnetic term ($J_A < 0$). The
potential interaction is a Coulombic repulsion term between the unpaired spins, which always result in a ferromagnetic contribution to the overall J. Kinetic interactions arise from transferring and delocalizing the unpaired electrons, which are virtually shown as mixing charge transfer excited states into the ground states. This can lead to either ferromagnetic or antiferromagnetic contribution depending on the bridging geometry and electronic configurations of the molecule of interest. This kinetic interaction has been shown, according to Anderson, Goodenough-Kanamori, Coronado, Weihe and Güdel, as the combination of several charge transfer processes between (1) half-occupied and half-occupied orbitals, (2) half-occupied and empty orbitals, (3) full-occupied and half-occupied orbitals, and (4) full-occupied and empty orbitals (Table 1, equation 1-4).

The first situation (equation 1) shows interactions between two delocalized and unpaired electrons which result in an antiferromagnetic contribution. In most molecular systems, this half-to-half transfer interaction is the dominant term for the kinetic exchange. In other situations relevant to this work (equation 2, equation 3 and some cases of equation 4), the relatively smaller ferromagnetic interactions can be observed (with a pre-factor of I'). For a species where J is dominant by kinetic exchange, antiferromagnetic coupling is most likely to be observed due to the contribution of the half-to-half transfer being larger than the other transfer interactions. Systems with a relative long distance between the spin centers allow for the potential exchange term to be ignored. Oxido-bridged complexes satisfy this criteria and most oxido-bridged complexes are found to be antiferromagnetically coupled. However, strong ferromagnetic coupling can be obtained by controlling bridge geometries and electronic configurations, as predicted and shown experimentally in homo- and heterobimetallic oxido-bridged complexes.
In order to understand the ferromagnetic interactions that originate from kinetic exchange, it is important to further explore this model in respect to other metallic ions with different electronic configurations. In this work, we examine magnetic coupling for a series of heterometallic complexes with $d^x$-$d^1$ electronic configurations ($x = 5-9$). Consistent ferromagnetic $J$ values are observed for Mn$^{III}$O$^{IV}$ (3), Co$^{III}$O$^{IV}$ (5), Ni$^{III}$O$^{IV}$ (6), and Cu$^{III}$O$^{IV}$ (7), with $J$ equaling $+38.3$ cm$^{-1}$, $+39.0$ cm$^{-1}$, $+22.5$ cm$^{-1}$ and $+11.7$ cm$^{-1}$, respectively. Fe$^{II}$O$^{IV}$ (4) ($d^6$-$d^1$) is found to have a low spin Fe$^{II}$ center and therefore no exchange interactions are observed. Empirical parameters for the effective transfer integrals are determined based on systems with similar structural parameters (3, 5-6), resulting in $h'_{\pi\pi} I' = 58.5$ cm$^{-1}$ and $h'_{\sigma\sigma} I' = 88.1$ cm$^{-1}$. This represents the two major exchange paths based on $\pi$ ($h'_{\pi\pi}$) and $\sigma$ ($h'_{\sigma\sigma}$) orbital interactions for the M$\equiv$O$\equiv$V$^{IV}$ system. These empirical transfer integrals can be used to reproduce the $J$ value for exchange coupling in a previously observed $d^2$-$d^1$ Cr$^{III}$O$^{IV}$ molecule (1), and to estimate the $J$ values for other electronic configurations that currently lack experimental examples. We have previously utilized such a model to identify additional parameters important for exchange coupling, such as the molecular twist in $d^4$-$d^1$ Mn$^{III}$O$^{IV}$ (2). Here we used it to identify the influence of Jahn-Teller distortion on orbital ordering of $d^9$-$d^1$ Cu$^{II}$O$^{IV}$ (7). To our knowledge, this is the first study of the magnetic interactions between $d^1$ vanadium and late transition metals such as Fe, Co, Ni, and Cu in such $\mu$-oxido-bridged geometry. This allows an in-depth understanding of the origin of ferromagnetic coupling using a kinetic exchange model. Due to the relationship between kinetic exchange interactions in charge transfer processes, measuring such spin-spin...
interactions can serve as an indirect probe for magnetic interactions for d$^n$-d$^1$ charge transfer excited states.$^{74,75}$

6.3 Experimental

6.3.1 General procedures

All chemicals were purchased from VWR International, Sigma Aldrich, Alfa Aesar or TCI America and used without further purification. Attenuated total reflectance (ATR)-FTIR spectra were recorded with a Bruker Alpha ATR-FTIR. Magnetic susceptibilities were measured on a Quantum Design MPMS-XL7 SQUID Magnetometer. A saturation plot was measured at 2 K with the applied field being varied from 0~70000 oe. Temperature-dependent magnetic susceptibilities were performed from 2-300 K. Crystalline samples (ca. 10-30 mg) were loaded into gelcap/straw sample holders and mounted to the sample rod with Kapton tape for temperature dependence measurements. Multiple measurements were performed. The least-squares fittings were performed by minimizing the residual $R = \Sigma[(\chi T)_{obs} - (\chi T)_{calc}]^2/\Sigma(\chi T)_{obs}^2$. The $g_{\text{Mn}}$ and $g_{\text{V}}$ values for 3 are restricted to the range of 1.9-2.1 to avoid overfitting. Diamagnetic correction -5.86 $\times$ 10$^{-4}$ emu/mol is applied to 4. The fitting results (such as g-factor, $\theta$ and $J$) from these separate data sets are consistent. The reported errors are based on several separate fitting results from different data sets. 3 is prepared according to previously reported approach using (omtaa)V═O.

6.3.2 X-Ray crystallography

Crystals were mounted on MiTeGen mounts and cooled to 100 K. X-ray intensity data were measured on a Bruker-Nonius X8 Kappa APEX II system equipped with a graphite monochromator and a MoK$\alpha$ fine-focus sealed tube ($\lambda = 0.71073$ Å). Unit cell dimensions were determined from symmetry constrained fits of the reflections. Frames were integrated
with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the multi-scan method (SADABS). Structures were solved using direct methods (Bruker XS) and refined using the Bruker SHELX 2013 software package using full-matrix least-squares refinement on F. All non-hydrogen atoms were identified in the original solution, or located from the difference map from refinement results. Hydrogen atoms were placed at idealized positions and allowed to ride on the nearest non-H atom. Figures of the molecular structures were created using Olex².

6.4 Result and discussion

6.4.1 Magnetic measurement

The sign and magnitude of magnetic exchange coupling J for 3-7 are determined through measurements of temperature-dependent magnetic susceptibility and the variable-field magnetization. The expressions derived from Heisenberg-Dirac-Van Vleck Hamiltonian expression⁷⁷ (equation 5) based on $H = -2J S_1 \cdot S_2$ and Brillouin function (equation 6) are used to fit the magnetic data. In the final equations, zero-field splitting (D), Weiss constant ($\theta$) and anisotropic g tensors have been taken into consideration wherever required. Magnetic properties of two previously reported species, d¹-d³ (omtaa)V═O→Cr(TFMP)Cl (1) and d¹-d⁴ (omtaa)V═O→Mn(TMP)SbF₆ (2) are included for comparison.

$$\chi = \frac{Ng^2 \beta^2}{3k_B T} \sum S(S+1)(2S+1)e^{\left(-\frac{E_s}{k_B T}\right)} \sum (2S+1)e^{\left(-\frac{E_s}{k_B T}\right)}$$  

(5)
\[ \frac{M}{N \mu_B} = g S B_j(x) \]

\[ B_j(x) = \frac{2S+1}{2S} \coth\left(\frac{2S+1}{2S} \times \frac{g \mu_B S}{k_B} \frac{H}{T}\right) - \frac{1}{2S} \coth\left(\frac{1}{2S} \times \frac{g \mu_B S}{k_B} \frac{H}{T}\right) \]

\[ \chi_M = \frac{N \beta^2}{3k_B(T - \theta)} \left(30g_2^2 + 84g_3^2 \left(e^{\frac{6J}{k_B T}}\right)\right) + C, \quad g_2 = \frac{7g_{Mn} - g_v}{6}, \quad g_3 = \frac{5g_{Mn} + g_v}{6} \]
As shown in Figure 6.1, the magnetic susceptibility of 3 was measured at 0.7 T in a temperature range of 2-300 K. The product of molar magnetic susceptibility and temperature ($\chi T$) of species 3 arises monotonically to a maximum value at about 50 K and retains a relative plateau until 15 K. The $\chi T$ value then decreases on further cooling due to weak intermolecular interactions and zero-field-splitting. The maximum $\chi T$ value for 3 is found to be 5.7 emu·K/mol, which is in agreement with the spin-only magnetic moments for paramagnetic centers with $S = 3$ and a previously reported analogue\textsuperscript{45}. This result is in line with variable-field susceptibility measurements, where a fit of the Brillouin function (equation 6) further confirms that the ground state of 3 has spin values of $S = 3$. The final expression for fitting $\chi T$-T plot is given as equation 7, where $N$ is Avogadro's number, $k_B$ is the Boltzmann constant, $T$ is the temperature, $\beta$ is the Bohr magneton, $\theta$ is the Weiss constant, $g_2$ and $g_3$ represent the electron g-factor for $S = 2$ and $S = 3$ states, $C$ represents the total contribution of temperature-independent-paramagnetic susceptibility (TIP) and diamagnetic susceptibility. Using this equation, the best fitting results are shown as $J = +38.3 \pm 0.8$ cm$^{-1}$, $\theta = -0.27 \pm 0.03$ K, $g_{Mn} = 1.93 \pm 0.01$, $g_V = 2.10 \pm 0.01$, $C = -8.39 \pm 0.21 \times 10^{-4}$ emu/mol, and $R^2 = 0.9999$. 
Figure 6.2 Temperature-dependent magnetic susceptibility ($\chi_T$ vs $T$) and variable-field magnetization at 2 K (in-set) for 4. Diamagnetic susceptibility has been corrected according to Pascal constants.$^{78}$ The simulated Brillouin function is plotted with $S = 1/2$ and $g = 2.00$ for comparison.

The magnetic properties of 4 was characterized and depicted in Figure 6.2. Due to the weak magnetization response in the range of 200–300 K, magnetic susceptibility was measured in the range of 2–200 K, where the $\chi_T$ values retain close to 0.29 emu·K/mol between 200 K and 10 K and then continue to decrease when T is lower than 10 K. This $\chi_T$ is found to be closed to the spin-only magnetic moments for paramagnetic centers with $S = 1/2$. This result suggests that the d$^6$ Fe$^{II}$ center of 4 has the low spin electronic configuration, and magnetization response is from d$^1$ V$^{IV}$. The result of variable-field magnetization at 2K supports this assignment as well, showing the number of unpaired spins close to $S = 1/2$. 
In the case of 5, ferromagnetic coupling is observed. As shown in Figure 6.3, the $\chi_T$ value increases monotonically and reaches its maximum point of 3.05 emu·K/mol at 65 K, which is consistent the spin-only magnetic moments for paramagnetic centers with $S = 2$. However, the $\chi_T$ value decreases dramatically in the range of 2~50 K, which is mainly due to the zero field splitting. This is also in line with other bimetallic species containing Co$^{II}$. In order to take the zero filed splitting into consideration, the Hamiltonian containing anisotropic interaction (equation 8) is used. The final expression (equation 9) is used to fit magnetic data, showing $J = +39.0 \pm 2.0$ cm$^{-1}$, $\theta = -0.57 \pm 0.04$ K, $g_{av} = 2.08 \pm 0.01$, $C = -1.24 \pm 0.14 \times 10^{-4}$ emu/mol, $D = 1.20 \pm 0.14$, and $R^2 = 0.9981$.

![Figure 6.3](image)

**Figure 6.3** Temperature-dependent magnetic susceptibility ($\chi_T$ vs $T$) and variable-field magnetization at 2 K (in-set) for 5. The simulated Brillouin function is plotted with $S = 2$ and $g = 2.00$ for comparison.
\[ \hat{H}_{ab} = -2J_{ab} \hat{S}_a \hat{S}_b + D(M_f^2 - \frac{1}{3} S_{tot}(S_{tot} + 1)) \]  

(8)

\[
\chi_M = \frac{N\beta^2 g^2}{3k_B T} \left( \frac{6J+2D}{k_B T} + \frac{6J+D}{k_B T} + \frac{2D}{3k_B T} \right) \left( \frac{\frac{1}{3}D}{k_B T} + \frac{6J-2D}{k_B T} + \frac{2D}{3k_B T} + \frac{6J+D}{k_B T} + \frac{6J+2D}{k_B T} \right)
\]  

(9)

The magnetic behavior of 6 is depicted in Figure 6.4, showing ferromagnetic coupling in d⁸-d¹ Ni³⁺O³⁴⁺ species as well. The \( \chi_T \) value increases monotonically and reaches its maximum point of 2.28 emu·K/mol at around 20 K, which is consistent with the spin-only magnetic moments for paramagnetic centers with \( S = \frac{3}{2} \). This assignment is also in line with the result of variable-field magnetization (Figure 6.4, in-set).

**Figure 6.4** Temperature-dependent magnetic susceptibility (\( \chi_T \) vs T) and variable-field magnetization at 2 K (in-set) for 6. The simulated Brillouin function is plotted with \( S = \frac{3}{2} \) and \( g = 2.00 \) for comparison.
The equation 10 is used for fitting the magnetization behavior, resulting in $J = +22.5 \pm 0.4$ cm$^{-1}$, $\theta = -0.61 \pm 0.01$ K, $g_{av} = 2.25 \pm 0.01$, $C = -1.10 \pm 0.05 \times 10^{-3}$ emu/mol and $R^2 = 0.9996$.

$$\chi_M = \frac{N\beta^2g^2}{3k_B T} \left( \frac{3J}{k_B T} \right) \left( \frac{3J}{k_B T} \right) \left( 4 + 8e^{\frac{3J}{k_B T}} \right)$$  

(10)

The magnetic properties of d$^1$-d$^1$ Cu$^{II}$O$^{II}$ (7) is also studied and depicted in Figure 6.5. The $\chi_T$ value increases slowly with the decrease of temperature. The maximum value of 1.10 emu·K/mol at about 10 K is obtained, which is consistent the spin-only magnetic moments for paramagnetic centers with $S = 1$. According to equation 11, the best fitting results of $J = +11.6$ $\pm 0.1$ cm$^{-1}$, $\theta = -0.07 \pm 0.01$ K, $g_{av} = 1.83 \pm 0.02$, $C = -4.30 \pm 0.03 \times 10^{-4}$ emu/mol and with $R^2 = 0.9995$ are obtained.

$$\chi_M = \frac{N\beta^2g^2}{3k_B T} \left( 1 + 6e^{\frac{2J}{k_B T}} \right) \left( 1 + 3e^{\frac{2J}{k_B T}} \right)$$  

(11)
Figure 6.5 Temperature-dependent magnetic susceptibility ($\chi T$ vs T) and variable-field magnetization at 2 K (in-set) for 6. The simulated Brillouin function is plotted with $S = 1$ and $g = 1.96$ for comparison.

6.4.2 Determination of transfer integrals

According to model developed by Weihe and Güdel, the theoretical expresses for $V^{IV}$–O–M complexes with different electronic configurations can be derived according the corresponding transfer integrals based to their electronic configurations (Table 6.2). Suggested by this work, the theoretical expresses can be simplified as equation 19-25 (Table 6.4). As shown in Table 6.3, species of 1-7 all demonstrate relative linear bridging geometries showing bending angle of $163.0^\circ$–$179.1^\circ$. The transfer integrals $h'_{yy}$ and $h'_{xx}$, which are determined by weakly interacting $d_{xy} - d_{xy}$ and $d_{x^2-y^2} - d_{x^2-y^2}$, are believed to be small and can be neglected. Previously study also suggested that the transfer integral $h'_{y\theta}$, which is determined by the
overlap of $d_{zx} - d_{z^2}$, can be ignored when bridging geometry is close to linear. The transfer integrals $h'_{\eta\eta}$ and $h'_{\xi\xi}$ are similar magnitude in such linear geometry and can be assumed to be the same. Therefore, we have assumed $h'_{\eta\eta} = h'_{\xi\xi}$ and neglected transfer integrals of $h'_{\zeta\zeta}$, $h'_{\epsilon\epsilon}$, and $h'_{\eta\theta}$ in the following discussions to reduce the parameters involved in our model (Table 6.4).

Table 6.2 Expressions for the kinetic exchange interaction of $J$

<table>
<thead>
<tr>
<th>m,n</th>
<th>$d^m$</th>
<th>$d^n$</th>
<th>$J_{\text{calc}}^a$</th>
<th>Label</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,3</td>
<td>$\zeta$</td>
<td>$\zeta\eta\xi$</td>
<td>$-\frac{2}{3} h'<em>{\zeta\zeta} + \frac{1}{3} h'</em>{\eta\eta} I + \frac{1}{3} h'<em>{\xi\xi} I' + \frac{1}{3} h'</em>{\eta\theta} I'$</td>
<td>(12)</td>
</tr>
<tr>
<td>1,4</td>
<td>$\zeta$</td>
<td>$\zeta\eta\xi\theta$</td>
<td>$-\frac{1}{2} h'<em>{\zeta\zeta} + \frac{1}{4} h'</em>{\eta\eta} I + \frac{1}{4} h'<em>{\xi\xi} I' + \frac{1}{4} h'</em>{\eta\theta} I'$</td>
<td>(13)</td>
</tr>
<tr>
<td>1,5</td>
<td>$\zeta$</td>
<td>$\zeta\eta\xi\theta\epsilon$</td>
<td>$-\frac{2}{5} h'<em>{\zeta\zeta} + \frac{1}{5} h'</em>{\eta\eta} I + \frac{1}{5} h'<em>{\xi\xi} I' + \frac{1}{5} h'</em>{\eta\theta} I'$</td>
<td>(14)</td>
</tr>
<tr>
<td>1,6</td>
<td>$\zeta$</td>
<td>$\zeta^2\eta\xi\theta\epsilon$</td>
<td>$h'<em>{\zeta\zeta} I' + \frac{1}{4} h'</em>{\eta\eta} I + \frac{1}{4} h'<em>{\xi\xi} I' + \frac{1}{4} h'</em>{\eta\theta} I'$</td>
<td>(15)</td>
</tr>
<tr>
<td>1,7</td>
<td>$\zeta$</td>
<td>$\zeta^2\eta^2\xi\theta\epsilon$</td>
<td>$h'<em>{\zeta\zeta} I' - \frac{1}{4} h'</em>{\eta\eta} I + \frac{1}{3} h'<em>{\xi\xi} I' - \frac{1}{4} h'</em>{\eta\theta} I'$</td>
<td>(16)</td>
</tr>
<tr>
<td>1,8</td>
<td>$\zeta$</td>
<td>$\zeta^2\eta^2\xi^2\theta\epsilon$</td>
<td>$h'<em>{\zeta\zeta} I' - \frac{1}{6} h'</em>{\eta\eta} I - \frac{1}{6} h'<em>{\xi\xi} I' - \frac{1}{6} h'</em>{\eta\theta} I' + \frac{1}{2} h'_{\epsilon\epsilon} I'$</td>
<td>(17)</td>
</tr>
<tr>
<td>1,9</td>
<td>$\zeta$</td>
<td>$\zeta^2\eta^2\xi^2\theta^2\epsilon$</td>
<td>$+ h'<em>{\zeta\zeta} I' + h'</em>{\epsilon\epsilon} I'$</td>
<td>(18)</td>
</tr>
</tbody>
</table>

$^a$ The effective parameters $\frac{h'_{ij}}{U} = h'_{ij}$ and $\frac{I}{U} = I'$ are used as defined from previous work. Orbitals are represented as $\zeta$ (xy), $\eta$ (xz), $\xi$ (yz), $\theta$ (z$^2$), and $\epsilon$ (x$^2$-y$^2$). Expressions are derived from the one-electron transfer interactions from equation 1-4.
<table>
<thead>
<tr>
<th>System</th>
<th>V-O (Å)</th>
<th>M-O(Å)</th>
<th>V-O-M(°)</th>
<th>Torsion(°)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.640</td>
<td>1.964</td>
<td>179.1</td>
<td>2.6</td>
<td>44</td>
</tr>
<tr>
<td>2</td>
<td>1.654</td>
<td>2.080</td>
<td>163.0</td>
<td>39.3</td>
<td>45</td>
</tr>
<tr>
<td>3</td>
<td>1.647</td>
<td>2.046</td>
<td>166.0</td>
<td>2.3</td>
<td>This work</td>
</tr>
<tr>
<td>4</td>
<td>1.657</td>
<td>1.956</td>
<td>167.4</td>
<td>4.1</td>
<td>23</td>
</tr>
<tr>
<td>5</td>
<td>1.648</td>
<td>2.024</td>
<td>168.1</td>
<td>3.1</td>
<td>23</td>
</tr>
<tr>
<td>6</td>
<td>1.644</td>
<td>2.034</td>
<td>168.0</td>
<td>3.3</td>
<td>23</td>
</tr>
<tr>
<td>7</td>
<td>1.651</td>
<td>1.953</td>
<td>170.7</td>
<td>6.2</td>
<td>23</td>
</tr>
</tbody>
</table>
Table 6.4. Expressions for the kinetic exchange interaction of J in relative linear geometry

<table>
<thead>
<tr>
<th>m,n</th>
<th>d&lt;sup&gt;m&lt;/sup&gt;</th>
<th>d&lt;sup&gt;n&lt;/sup&gt;</th>
<th>J&lt;sub&gt;calc&lt;/sub&gt;&lt;sup&gt;a,b&lt;/sup&gt;</th>
<th>Label</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,3</td>
<td>ζ</td>
<td>ζηξζ</td>
<td>+ \frac{2}{3} h'_{\eta\eta} I'</td>
<td>(19)</td>
</tr>
<tr>
<td>1,4</td>
<td>ζ</td>
<td>ζηξθζ</td>
<td>+ \frac{1}{2} h'<em>{\eta\eta} I' + \frac{1}{4} h'</em>{\theta\theta} I'</td>
<td>(20)</td>
</tr>
<tr>
<td>1,5</td>
<td>ζ</td>
<td>ζηξθεζ</td>
<td>+ \frac{1}{5} h'<em>{\eta\eta} I' + \frac{1}{4} h'</em>{\theta\theta} I'</td>
<td>(21)</td>
</tr>
<tr>
<td>1,6</td>
<td>ζ</td>
<td>ζ&lt;sup&gt;2&lt;/sup&gt;ηξθεζ</td>
<td>+ \frac{1}{2} h'<em>{\eta\eta} I' + \frac{1}{4} h'</em>{\theta\theta} I'</td>
<td>(22)</td>
</tr>
<tr>
<td>1,7</td>
<td>ζ</td>
<td>ζ&lt;sup&gt;2&lt;/sup&gt;η&lt;sup&gt;2&lt;/sup&gt;ξθεζ</td>
<td>+ \frac{1}{12} h'<em>{\eta\eta} I' + \frac{1}{3} h'</em>{\theta\theta} I'</td>
<td>(23)</td>
</tr>
<tr>
<td>1,8</td>
<td>ζ</td>
<td>ζ&lt;sup&gt;2&lt;/sup&gt;η&lt;sup&gt;2&lt;/sup&gt;ξ&lt;sup&gt;2&lt;/sup&gt;θεζ</td>
<td>- \frac{1}{3} h'<em>{\eta\eta} I' + \frac{1}{2} h'</em>{\theta\theta} I'</td>
<td>(24)</td>
</tr>
<tr>
<td>1,9</td>
<td>ζ</td>
<td>ζ&lt;sup&gt;2&lt;/sup&gt;η&lt;sup&gt;2&lt;/sup&gt;ξ&lt;sup&gt;2&lt;/sup&gt;θεζ</td>
<td>0</td>
<td>(25)</td>
</tr>
</tbody>
</table>

<sup>a</sup> The effective parameters \( \frac{h_{ij}^2}{U} = h'_{ij} \) and \( \frac{I}{U} = I' \) are used as defined from previous work.

<sup>b</sup> Expressions are derived from the one-electron transfer integrals: equation 1-4.

In order to extract the transfer integrals, the experimental results of 3, 6 and 7 are used. As noticed in the expresses in Table 6.3, they have similar structure parameters including bond lengths (2.024-2.046 Å) and bending degree (166.0-168.1°). Therefore, we use them to perform linear least squares regression to their experimental J values. The least squares fit to those linear models shown in equation 21, 23-24 yields the effective transfer integrals of \( h'_{\eta\eta} I' = 58.5 \) cm<sup>-1</sup> and \( h'_{\theta\theta} I' = 88.1 \) cm<sup>-1</sup>, representing the transfer interaction through π and θ directions. It is worth noting that, the transfer integrals are affected by bending degree. The
angular overlap model has been used to qualitatively estimate the exchange interactions.\textsuperscript{65,66,82,83} We also include such model, however, due the bending degree are very closed to linear, closed fitting results are obtained.

6.4.3. Estimation of J of different electronic configurations

According to the obtained transfer integrals, we estimate the J values with different electronic configurations and the results are summarized in Table 6.5. As can be noted, the magnitude of previously reported ferromagnetic interaction in 1 ($J_{\text{exp}} = +42.5$ cm$^{-1}$) was reproduced, with $J_{\text{calc}} = +39.0$ cm$^{-1}$ being computed. Application of this approach allows the determination of theoretical J values not obtained in this work, such as d$^1$-d$^6$ V$^{IV}$-Fe$^{II}$ with high spin electronic configuration. ($J_{\text{calc}} = +51.3$ cm$^{-1}$). The theoretical value of d$^1$-d$^6$ V$^{IV}$-Mn$^{III}$ couple is not consistent with the unusual small experimental result of 2, which has been attributed to the molecular twist.\textsuperscript{45} Interestingly, the computation result differs from the experiment result of 7 as well. A noticeable large ferromagnetic interaction was observed for 7 ($J_{\text{exp}} = +11.7$ cm$^{-1}$), which is in contrast with the prediction. The proposed expression (equation 19) is believed to be small owing to their small transfer integrals of $h'_{\pi}$ and $h'_{\alpha\pi}$, which lack the appropriate orbital overlap.
Table 6.5 Comparison between calculated and experimental results.

<table>
<thead>
<tr>
<th>System</th>
<th>( J_{\text{calc}} ) (cm(^{-1}))</th>
<th>( J_{\text{exp}} ) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>+39.0</td>
<td>+42.5</td>
</tr>
<tr>
<td>2</td>
<td>+51.3</td>
<td>+2.6</td>
</tr>
<tr>
<td>3</td>
<td>+41.0</td>
<td>+38.3</td>
</tr>
<tr>
<td>4</td>
<td>+51.3</td>
<td>N.A.</td>
</tr>
<tr>
<td>5</td>
<td>+34.3</td>
<td>+39.0</td>
</tr>
<tr>
<td>6</td>
<td>+24.6</td>
<td>+22.5</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>+11.7</td>
</tr>
</tbody>
</table>

This ferromagnetic interaction of 7 is further explained. As shown in Figure 6.6, due to the Jahn-Teller effect, the Cu center falls in a pentacoordinate environment. The \( d_{x^2-y^2} \) orbital of Cu lies parallel to the direction of Cu–O bond, forming a \( \sigma \) type interaction with the \( p_z \) orbital of oxygen. This \( p_z \) orbital also forms strong interaction with the \( d_{z^2} \) in the vanadium center. Similarly the \( d_{xy} \) orbital forms \( \pi \) bonding with \( p_x \) orbital in the oxygen, interaction with to the \( d_{xz} \) in the vanadium. As noticed in Table 6.1, such two pathways should result in ferromagnetic coupling, and theoretical expression should be \( J_{\text{calc}} = +h'\psi_\eta I' + h'_0 I' \). This Jahn-Teller distortion is found to an enhancement of the ferromagnetic interaction by increasing of effective overlap between these paramagnetic centers through \( \sigma \) and \( \pi \) pathways.
Table 6.6 Schematic demonstration of proposed kinetic exchange pathways of 7. (A) The $[\frac{1}{2}]_A \rightarrow [0]_B$ transfer interaction based on $\sigma$ overlap between Cu($d_{x^2-y^2}$), O($p_z$) and V($d_{z^2}$). (B) The $[1]_A \rightarrow [\frac{1}{2}]_B$ transfer interaction based on $\pi$ overlap between Cu($d_{xy}$), O($p_x$) and V($d_{xz}$). The final expression derived from these transfer integrals is given as $J_{\text{calc}} = +h'_{\tilde{\chi}'\eta} I' + h'_{\tilde{\rho}'} I'$. 

6.5 Conclusion

As the summary, we have shown the ferromagnetic coupling is observed in serious of $d^1$-$d^5$, $V^{IV}$–O–M complexes. This result is rationalized using models based on kinetic exchange interaction and nice agreement between experiment and calculation are obtained. The transfer integrals of $\pi$ ($h'_{\eta\eta} I' = 58.5$ cm$^{-1}$) and $\sigma$ orbitals ($h'_{\tilde{\rho}\tilde{\rho}} I' = 88.1$ cm$^{-1}$) are obtained and can be used to successfully reproduce and estimate the ferromagnetic coupling through this oxido-bridged geometry with other electronic configurations. The unusual ferromagnetic coupling of 7 is further rationalized as the Jahn-Teller distortion, which alters the orientations of its magnetic orbitals and increases $\pi$-$\pi$ and $\sigma$-$\sigma$ exchange interactions.
6.6 Supporting information

![Figure 6.51. X-ray crystal structure of 3. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms, solvent molecules and anions are omitted for clarity.](image)

A clear light orange needle-like specimen of C_{58}H_{57}Cl_{6}MnN_{9}O_{7}S_{2}V, approximate dimensions 0.839 mm × 0.169 mm × 0.145 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

A total of 994 frames were collected. The total exposure time was 31.12 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 88438 reflections to a maximum θ angle of 25.681° (0.82 Å resolution), of which 11512 were independent (average redundancy 7.67, completeness = 99.9 %, Rint = 4.63%, Rsig = 3.43%) and 8910 (77.40%) were greater than 2σ(F^2). The final cell constants of a = 13.1778(5) Å, b = 13.7937(4) Å, c =
18.4058(2) Å, α = 108.470(2)°, β = 92.159(2)°, γ = 105.087(2)°, volume = 3037.44(19) Å³, are based upon the refinement of the XYZ-centroids of 9946 reflections above 2σ(I) with 4.706° < 2θ < 52.424°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.9360.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P-1, with Z = 2 for the formula unit, C₅₈H₅₇Cl₂F₆MnN₉O₇S₂V. The final anisotropic full-matrix least-squares refinement on F² with 823 variables converged at R₁ = 6.18 %, for the observed data and wR₂ = 17.61 % for all data. The goodness-of-fit was 1.048. The largest peak in the final difference electron density synthesis was 1.745 e-/Å³ and the largest hole was -1.346 e-/Å³ with an RMS deviation of 0.110 e-/Å³. On the basis of the final model, the calculated density was 1.473 g/cm³ and F(000), 1384.0 e⁻.

SQUEEZE of PLATON was applied to deal with disordered solvent. Analysis revealed 95 cubic angstroms of void space and 6 electrons house therein. This approximates to 1 H₂O per unit cell, or 0.5 per formula unit.

**Table 6.S1.** Ordinary least squares result for transfer integrals.

|                  | Fitting Result | Estimate Std | Error  | Pr(>|t|) |
|------------------|----------------|--------------|--------|----------|
| \( h'_{\eta\eta} I' \) | 58.479         | 11.274       | 5.187  | 0.1212   |
| \( h'_{\delta\delta} I' \) | 88.140         | 9.387        | 9.390  | 0.0675   |

Multiple \( R^2 = 0.9902 \), adjusted \( R^2 = 0.9706 \), p-value = 0.09899

6.7 References


(13) Han, H.; Frei, H. Microporous Mesoporous Mater. 2007, 103, 265.


CHAPTER 7

Synthesis, Structure and Olefin Epoxidation of Manganese Porphyrins with Targeted Axial Modifications

This manuscript is prepared to submit to Inorg. Chem.

*Tao Huang, Kyle B. Resco, Xinyuan Wu, Jennifer L. Roizen, Walter W. Weare* and Roger D. Sommer

Huang, T performed all general characterization. He work with Kyle B. Resco in the epoxidation experiment. He worked with Sommer, R. D. to conduct X-ray diffraction experiment. The synthesis was performed by Huang, T, Kyle B. Resco and Wu, X.

Department of Chemistry, North Carolina State University;

Raleigh, NC, 27695-8204

Department of Chemistry, Duke University,

Durham, NC, 27708, USA
7.1 Abstract

Manganese(III) porphyrin with targeted mono- and bis-axial substituents are synthesized, structurally characterized and applied as catalysts for olefin epoxidation. Different target groups such as titanyl (Ti═O, 1-2), vanadyl (V═O, 3-5), triphenylphosphine oxide (P═O, 6-7) and imidazole (Im, 8-13) are utilized as axial ligands to generate penta- and hexacoordinate manganese (III) porphyrins. X-ray structures of mono-axially substituted (1, 4, 6, 9-10) species were obtained, exhibiting non-planar saddle-shaped geometries with Mn-X (X, axially bonded atom) bond lengths of 2.034 Å, 2.080 Å, 2.059 Å, and 2.185 Å for Ti═O, V═O, P═O and Im, respectively. On the contrary, structures of bis-axially substituted (5, 7, 12-13) species demonstrate non-distorted planar manganese(III) porphyrins with longer Mn-X bond lengths of 2.251 Å, 2.162 Å, and 2.262~2.277 Å for V═O, P═O, and Im, respectively. The effectiveness of penta- and hexacoordinate manganese(III) porphyrins as the epoxidation catalysts are evaluated using cyclohexene with iodosylbenzene as the oxidant. Mono-axially substituted species demonstrate superior reactivity and selectivity over bis-axially substituted complexes. Such cationic mono-axially substituted manganese(III) porphyrins (1, 4, 6 and 8) also show excellent yield and selectivity in the epoxidation of trans-β-methylstyrene (up to 97.2% epoxide formation in 0.5 h) and cis-β-methylstyrene (>33:1 cis:trans for 6) in mild conditions. Moreover, only 6 is found to promote the in situ isomerization of trans- and cis-β-methylstyrene oxide to form Meinwald rearranged carbonyl species. This is attributed to the ability of the P═O group in stabilizing the hexacoordinate epoxide-manganese(III) porphyrin adducts.
7.2 Introduction

The metalloporphyrin complexes of first row transition metals have been extensively studied in catalyzing oxidation reactions of hydrocarbons.\textsuperscript{1-5} Due to the structural relationship with naturally occurring enzymes,\textsuperscript{3,4,6-10} wide-ranging efforts have been paid to elucidate the mechanisms and intermediates involving in reactions.\textsuperscript{8,9,11-21} The manganese porphyrins have been employed as catalysts in olefin epoxidation, showing superior effectiveness and stability.\textsuperscript{19} Such catalysts are continuing to attract attention from border audiences in doing other reactions such as halogenation\textsuperscript{22} and cycloaddition.\textsuperscript{23}

The axial ligands in these heme-like systems are known to be crucial in oxidant binding,\textsuperscript{24,25} oxidant activating,\textsuperscript{12} and oxygen atom transferring.\textsuperscript{7} The targeted modification on manganese porphyrin in the axial position would potentially lead to the change in reactivities of these substituents in the \textit{trans} position\textsuperscript{24,26} (such as oxygen or halogens) and Lewis acidity of the metal center. Recent review in manganese porphyrins\textsuperscript{22} and mechanism studies of high valent manganese porphyrinoid species\textsuperscript{27} also put emphasis on the importance of the axial ligands. It is possible that reactive intermediate may vary dramatically due to different axial modification.\textsuperscript{21}

It is known that the pentavalent O=Mn\textsuperscript{V}(L/X)(Por)\textsuperscript{15,28} (L stands for neutral axial ligands and X stands for anionic axial ligands) is the main reactive oxidant in olefin oxidation. Neutral ligands such as imidazole, Ph\textsubscript{3}PO, or N-Oxide have also been studied as co-catalysts in metalloporphyrin or salen complexes to improve turnover rates and product selectivities.\textsuperscript{12,29-32} One reason for this enhancement of reactivity is explained by the donating ability of axial ligand, which can lead to the lengthening and weakening of the \textit{trans} metal-oxygen bond in O=Mn\textsuperscript{V}(Por).\textsuperscript{9} The lengthening of metal-oxygen bond is also consistent with the experimental
result in high valent manganese oxo species.\textsuperscript{27,28} However, due to the high reactivity of O=Mn\textsuperscript{V}(L/X)(Por) species, spectroscopic and structural studies have been focused on other alternative high valent O=Mn\textsuperscript{V} complexes,\textsuperscript{27,28} even though these species lack the ability to catalyze oxidative reactions effectively. Pentacoordinate trivalent Mn\textsuperscript{III}(L/X)(Por) is well documented as a precursor, and is believed to be oxidized \textit{in situ} to form the reactive high valent O=Mn\textsuperscript{V}(L/X)(Por).\textsuperscript{15,17,19} Thus, the structural study and spectroscopic characterization of the pentacoordinate trivalent manganese porphyrin might be useful to predict the reactivity of the high valent O=Mn\textsuperscript{V}(L/X)(Por) intermediate.

Addition of large excess amount (> 20 fold) of the axial ligands\textsuperscript{29,30,33,34} or anchoring the donating group in porphyrin ligand via synthetic approach remain the major approaches to achieve axially ligated metalloporphyrin. Since pentacoordinate manganese porphyrins are the precursor which will interact with oxidant and substrate, adding excess axial ligand might result in reducing the turnover rate due to formation of less reactive hexacoordinate adducts.\textsuperscript{29,35} Thus, target synthesis of pentacoordinate cationic manganese porphyrins with effective donors (such as imidazole or Ph\textsubscript{3}PO) as axial ligand may provide the direct effective precursor and facilitate the subsequent reactions. To our best knowledge, only few examples of cationic pentacoordinate manganese porphyrin has been reported structurally\textsuperscript{36,37} and few of them has been applied in catalytic reactions.

Our group has been focusing on the target synthesis of the metalloporphyrin with different axial modification.\textsuperscript{38,39} Despite the difficulty in the separation of penta- and hexacoordinante metalloporphyrin species,\textsuperscript{40} recent study suggests that the formation of axial substituents could be controllable in chromium porphyrin.\textsuperscript{39} These structures suggest the transition metallic oxide (Ti═O or V═O) can be used as axial substituents as well, exhibiting a shorter distance than
previously known imidazole\textsuperscript{41} or Ph\textsubscript{3}PO.\textsuperscript{42} The lability of chloride atom in the \textit{trans} position with significant bond elongation is observed.\textsuperscript{38,39} Therefore, such metallic oxo groups are included as axial substituents to study their influences on manganese porphyrin mediated oxygen atom transfer reactions.

In this work, we have successfully synthesized and structurally characterized cationic pentacoordinate Mn(L)(Por)\textsuperscript{+} and hexacoordinate Mn(L)\textsubscript{2}(Por)\textsuperscript{+}, where L = (tmtaa)Ti═O (Ti═O), (tmtaa)V═O/(omtaa)V═O (V═O), Ph\textsubscript{3}PO (P═O) and imidazole (Im). The monoaxial adducts are found to catalyze olefin (cyclohexene, \textit{tran/cis}-\textbeta-methylstyrene) epoxidation effectively using iodosylbenzene as the oxidant. The reactivity of catalysts were found to be influenced by the axial ligands with the reactivity order of Im > Ph\textsubscript{3}PO ∼ (tmtaa)Ti═O > (omtaa)V═O > (tmtaa)V═O for cyclohexene. Superior yield and selectivity for \textit{tran/cis}-\textbeta-methylstyrene epoxidation were achieved utilizing such cationic pentacoordinate species. Meanwhile, we found that only 6 (L = Ph\textsubscript{3}PO) can catalyze \textit{in situ} Meinwald rearrangement of \textit{tran/cis}-\textbeta-methylstyrene oxide to form rearranged carbonyl products. These results suggest the axial modification would dramatically enhance epoxidation reactivity, affect the intermediates in epoxide formation, and promote the reactivity of the Lewis acid induced epoxide rearrangement.

\textbf{7.3 Experimental}

\textbf{7.3.1 General}

All reactions were performed under an atmosphere of nitrogen in an Innovative Technology glovebox or using Schlenk techniques. All chemicals were purchased from VWR International, Sigma Aldrich, Alfa Aesar or TCI America and used without further purification. All solvents were stored over 4Å molecular sieves prior to use. Dichloromethane and pentane were sparged
with N\textsubscript{2} and dried over an alumina column using the method of Grubbs\textsuperscript{43}. Toluene was dried over purple sodium benzophenone ketyl, then vacuum transferred and freeze-pump-thawed before storing in Teflon-sealed Schlenk bombs. Acetonitrile was dried over CaH\textsubscript{2} and distilled prior to use. Attenuated total reflectance (ATR)-FTIR spectra were recorded with either a Bruker Vertex 80V infrared spectrometer equipped with a Platinum\textsuperscript{TM} Diamond ATR attachment or a Bruker Alpha ATR-FTIR. The ligands studied in this report are represented by the following abbreviations: TPP, tetraphenylporphyrin; TMP, tetrakis(4-methoxyphenyl)porphyrin TFP, tetrakis(4-fluorophenyl)porphyrin; tmtaa: 7,16-dihydro-6,8,15,17-tetramethylldibenzo[b,i][1,4,8,11]tetraazacyclotetradecine, omtaa: 7,16-dihydro-6,8,11,12,15,17,20,21-octamethyldibenzo[b,i][1,4,8,11]tetraazacyclotetradecine. The ligands were synthesized according to the reports of Weare and coworkers\textsuperscript{39} and Goedken and coworkers\textsuperscript{44}. (tmtaa)Ti═O, (tmtaa)V═O, (omtaa)V═O\textsuperscript{44} and Mn(TMP)SbF\textsubscript{6} were synthesized as previously reported. \textsuperscript{1}H-NMR were recorded on a Varian Mercury 400MHz spectrometer. Chemical shifts are reported with reference to solvent resonances \textsuperscript{1}H NMR (CDCl\textsubscript{3}:7.26 ppm). The epoxidation reactions were performed in J. Young NMR tubes and was monitored directly via \textsuperscript{1}H-NMR. A concentration of approximate 0.1 M olefin was prepared in CDCl\textsubscript{3} and mixed with the corresponding catalyst and oxidant. The typical ratio of catalyst [C] : substrate [S] : oxidant [O] is 5:100:200 unless otherwise mentioned. Due to low solubility in CDCl\textsubscript{3}, the mixture was ultrasonically mixed for 5 min at the beginning.

\textbf{7.3.2 Synthesis}

\textbf{Synthesis of Mn(Por)SbF\textsubscript{6}}

The synthesis is adapted from previous reports\textsuperscript{2}. In the glovebox, Mn(TPP)Cl (200.0 mg, 0.28 mmol) and NaSbF\textsubscript{6} (81.0 mg 0.31 mmol) were added to a 8 mL of 1:1 acetonitrile : toluene
mixture in a 50 mL Teflon-sealed Schlenk flask and heated at 80 °C for 12 h. The solution was then cooled slowly to room temperature and was filtered to remove NaCl. A fine green powder was obtained from the filtrate after removal of the solvent in vacuo. The final product was obtained after recrystallization via layered diffusion of pentane (15 mL) into a dichloromethane (3 mL) solution at -25 °C.

**Mn(TPP)SbF₆:** Yield after recrystallization: 244.5 mg, 95.3%. Anal. calc’d for C₄₄H₂₈F₆MnN₄Sb•CH₂Cl₂: C, 54.69; H, 3.06; N, 5.67. Found: C, 55.03; H, 3.16; N, 5.92. HRMS-ESI (M⁺) calc’d for C₄₄H₂₈MnN₄: 667.1689 Found: 667.1676.

**Mn(TFP)SbF₆:** Yield after recrystallization: 226.0 mg, 81.6%. Anal. calc’d for C₄₄H₂₄F₁₀MnN₄Sb•0.25CH₂Cl₂: C, 53.33; H, 2.48; N, 5.62. Found: C, 53.53; H, 2.52; N, 6.06. HRMS-ESI (M⁺) calc’d for C₄₄H₂₈MnN₄: 739.1312 Found: 739.1300.

**Synthesis of MnSbF₆TPPTiOTMTAA, (1)**

The synthesis of mono- and bis-axially substituted manganese(III) porphyrin is adapted from previous report.⁴⁵ In the glovebox, (tmtaa)Ti═O (50.0 mg, 0.12 mmol) and Mn(TPP)SbF₆ (111.2 mg 0.12 mmol) were dissolved in 5 mL dichloromethane in a 20 mL glass vial and stirred at room temperate for 5 min. A small amount of solution was dropped onto an ATR-FTIR sample holder and allow dry. The IR spectrum was then taken from this dried sample to monitor the reaction completeness using the disappearance of νTi═O at 930 cm⁻¹. When reaction is complete (c.a. 10 min), 15 ml pentane was slowly added onto this solution and stored in a -20 °C freezer for three days. Green crystalline solid was obtained after filtration. The final X-ray quality product was obtained after recrystallization via layered diffusion of pentane (2.5 mL) into a dichloromethane (1 mL) solution with 4 mg sample at -20 °C. Yield after recrystallization: 138.8 mg, 86.1%. ATR-FTIR νTi═O (cm⁻¹): 900(s). Anal. calc’d for
C$_{66}$H$_{50}$F$_{6}$MnN$_{8}$O$_{2}$SbTi•CH$_2$Cl$_2$: C, 57.70; H, 3.76; N, 8.03. Found: C, 57.26; H, 3.82; N, 8.38.

HRMS-ESI (M$^+$) calc’d for C$_{66}$H$_{50}$MnN$_{8}$OTi: 1073.2962, Found 1073.2925.

Synthesis of MnSbF$_6$TPP(TiOTMTAA)$_2$, (2)

The compound was synthesized and purified by following a procedure similar to that described above for 1 using two equivalents of (tmtaa)Ti═O (22.0 mg, 0.054 mmol), one equivalent of Mn(TPP)SbF$_6$ (24.5 mg 0.027 mmol). Yield after recrystallization: 35 mg, 75.0%. ATR-FTIR ν$_{Ti═O}$ (cm$^{-1}$): 905(s). Anal. calc’d for C$_{88}$H$_{72}$F$_{6}$MnN$_{12}$O$_2$SbTi$_2$•2CH$_2$Cl$_2$: C, 59.36; H, 4.14; N, 9.33. Found: C, 59.14; H, 4.10; N, 8.38. HRMS-ESI (M$^+$) calc’d for C$_{88}$H$_{72}$MnN$_{12}$O$_2$Ti$_2$: 1479.4235, Found: 1479.4198

Synthesis of MnSbF$_6$TPPVOTMTAA (3),

The compound was synthesized and purified by following a procedure similar to that described above for 1 using one equivalent of (tmtaa)V═O (20.0 mg, 0.049 mmol), one equivalent of Mn(TPP)SbF$_6$ (44.1 mg 0.049 mmol). Yield after recrystallization: 60.0 mg, 93.6%. ATR-FTIR ν$_{V═O}$ (cm$^{-1}$): 928(s). Anal. calc’d for C$_{66}$H$_{50}$F$_{6}$MnN$_{8}$O$_{2}$SbV•2CH$_2$Cl$_2$: C, 55.09; H, 3.67; N, 7.56. Found: C, 56.12; H, 3.43; N, 7.82. HRMS-ESI (M$^+$) calc’d for C$_{66}$H$_{50}$MnN$_{8}$OV: 1076.2922. Found 1076.2898.

Synthesis of Mn(TPP)SbF$_6$VOOTMTAA, (4)

The compound was synthesized and purified by following a procedure similar to that described above for 1 using one equivalent of (omtaa)V═O (22.5 mg, 0.048 mmol), one equivalent of Mn(TPP)SbF$_6$ (43.7 mg 0.048 mmol). Yield after recrystallization: 47.8 mg, 72.2%. ATR-FTIR ν$_{V═O}$ (cm$^{-1}$): 908(s). Anal. calc’d for C$_{70}$H$_{58}$F$_{6}$MnN$_{8}$O$_{2}$SbV•2CH$_2$Cl$_2$: C, 56.20; H, 4.06; N, 7.28. Found: C, 56.41; H, 4.06; N, 7.33. HRMS-ESI (M$^+$) calc’d for C$_{70}$H$_{58}$MnN$_{8}$OV: 1132.3548. Found 1132.3520.
Synthesis of Mn(TPP)SbF$_6$(VOOMTAA)$_2$ (5)

The compound was synthesized and purified by following a procedure similar to that described above for 1 using two equivalents of (omt aa)V═O (20.8 mg, 0.045 mmol), one equivalent of Mn(TPP)SbF$_6$ (20.2 mg 0.022 mmol). Yield after recrystallization: 39.2mg, 95%. An alternative the one-pot synthesis can be adapted from our previous report.$^{38,39}$ (omt aa)V═O (50.0 mg, 0.11 mmol), Mn(TPP)Cl (38.0 mg 0.055 mmol) and NaSbF$_6$ (15.4 mg, 0.060 mmol) were added to 5 mL of 1:1 acetonitrile:toluene mixture in a 50 mL Teflon-sealed Schlenk flask and heated at 80 °C for 12 h. The solution was then cooled slowly to room temperature and was filtered to remove side products. A fine green powder was obtained from the filtrate after removal of the solvent in vacuo. Yield after recrystallization: 67.5mg, 68%. The final X-ray quality product was obtained via similar approach as 1. ATR-FTIR $\nu_{\text{V}═\text{O}}$ (cm$^{-1}$): 909(s). Anal. calc’d for C$_{96}$H$_{88}$F$_6$MnN$_{12}$O$_2$SbV$_2$ •4CH$_2$Cl$_2$: C, 54.46; H, 4.41; N, 7.73. Found: C, 54.06; H, 4.51; N, 7.75. HRMS-ESI (M$^+$) calc’d for C$_{96}$H$_{88}$MnN$_{12}$O$_2$V$_2$: 1597.5408. Found 1597.5369.

Synthesis of Mn(TPP)SbF$_6$OPPh$_3$ (6)

The compound was synthesized and purified by following a procedure similar to that described above for 1 using one equivalent of Ph$_3$PO (21.6 mg, 0.078 mmol), one equivalent of Mn(TPP)SbF$_6$ (70.0 mg 0.78 mmol). Yield after recrystallization: 86.5 mg, 94.4%. The final X-ray quality product was obtained via similar approach as 1. ATR-FTIR $\nu_{\text{P}═\text{O}}$ (cm$^{-1}$): 1153(s). Anal. calc’d for C$_{62}$H$_{43}$F$_6$MnN$_4$OPsb: C, 63.02; H, 3.67; N, 4.74. Found: C, 62.26; H, 3.60; N, 4.37. HRMS-ESI (M$^+$) calc’d for C$_{62}$H$_{43}$MnN$_4$OP: 945.2550, Found 945.2523.

Synthesis of Mn(TPP)SbF$_6$(OPPh$_3$)$_2$ (7)

The compound was synthesized and purified by following a procedure similar to that described above for 1 using two equivalents of Ph$_3$PO (43.2 mg, 0.156 mmol) and one
equivalent of Mn(TPP)SbF$_6$ (70.0 mg 0.78 mmol). Yield after recrystallization: 96.5 mg, 85.2. The final X-ray quality product was obtained via similar approach as 1. ATR-FTIR $\nu_{P=O}$ (cm$^{-1}$): 1174(s). Anal. calc’d for C$_{80}$H$_{58}$F$_6$MnN$_4$O$_2$P$_2$Sb•CH$_2$Cl$_2$: C, 62.72; H, 3.91; N, 3.56. HRMS-ESI ([M-L]$^+$) calc’d for C$_{62}$H$_{43}$MnN$_4$OP: 945.2550, Found 945.2522. ([M]$^+$) calc’d for C$_{80}$H$_{58}$MnN$_4$O$_2$P$_2$: 1223.3410, Found 1223.3378.

Synthesis of Mn(TPP)SbF$_6$Imidazole (8)

The compound was synthesized and purified by following a procedure similar to that described above for 1 using one equivalent of imidazole (3 mg, 0.044 mmol) and one equivalent of Mn(TPP)SbF$_6$ (40.0 mg 0.044 mmol). Yield after recrystallization: 27.8 mg, 64.7%. ATR-FTIR $\nu_{NH}$ (cm$^{-1}$): 3422(w), $\nu_{Im}$ (cm$^{-1}$): 1538(w). Anal. calc’d for C$_{47}$H$_{32}$F$_6$MnN$_6$Sb: C, 54.57; H, 3.24; N, 7.96. Found: C, 54.97; H, 3.06; N, 8.47. HRMS-ESI (M$^+$) calc’d for C$_{47}$H$_{32}$MnN$_6$: 735.2064 Found 735.2046

Synthesis of Mn(TMP)SbF$_6$Imidazole (9)

The compound was synthesized and purified by following a procedure similar to that described above for 1 using one equivalent of imidazole (5.0 mg, 0.073 mmol) and one equivalent of Mn(TMP)SbF$_6$ (75.2 mg 0.073 mmol). Yield after recrystallization: 78.7 mg, 98.1%. The final X-ray quality product was obtained via similar approach as 1. ATR-FTIR $\nu_{Im}$ (cm$^{-1}$): 1532(w). Anal. calc’d for C$_{51}$H$_{40}$F$_6$MnN$_6$O$_4$Sb•2CH$_2$Cl$_2$: C, 50.46; H, 3.52; N, 6.66. Found: C, 49.22; H, 3.36; N, 7.13. HRMS-ESI (M$^+$) calc’d for C$_{51}$H$_{40}$MnN$_6$O$_4$: 855.2486. Found 855.2468

Synthesis of Mn(TFP)SbF$_6$Imidazole (10)

The compound was synthesized and purified by following a procedure similar to that described above for 1 using one equivalent of imidazole (5.0 mg, 0.073 mmol), one equivalent
of Mn(TFP)SbF₆ (71.6 mg 0.073 mmol). Yield after recrystallization: 54.8 mg, 71.5%. The final X-ray quality product was obtained via similar approach as 1. ATR-FTIR ν_{NH} (cm⁻¹): 3384(w), ν_{Im} (cm⁻¹): 1534(w). Anal. calc’d for C₄⁷H₂₈F₁₀MnN₆Sb•CH₂Cl₂: C, 51.09; H, 2.68; N, 7.45. Found: C, 51.77; H, 2.66; N, 7.59. HRMS-ESI (M⁺) calc’d for C₄⁷H₂₈F₄MnN₆: 807.1687. Found 807.1665.

Synthesis of Mn(TPP)SbF₆(Imidazole)₂ (11)

The compound was synthesized and purified by following a procedure similar to that described above for 4 using two equivalents of imidazole (5.3 mg, 0.078 mmol), one equivalent of Mn(TPP)SbF₆ (35.0 mg 0.039 mmol). Yield after recrystallization: 34.5 mg, 85.7%. ATR-FTIR ν_{NH} (cm⁻¹): 3411(m), ν_{Im} (cm⁻¹): 1532(m). Anal. calc’d for C₅₀H₃₆F₆MnN₈Sb•C₃H₄N₂: C, 57.47; H, 3.64; N, 12.65. Found: C, 56.10; H, 3.43; N, 12.27. HRMS-ESI ([M-L]⁺) calc’d for C₄⁷H₃₂MnN₆: 735.2064 Found 735.2053. ([M⁺]⁺) calc’d for C₅₀H₃₆MnN₈: 804.2516 Found 804.2650

Synthesis of Mn(TMP)SbF₆(Imidazole)₂ (12)

The compound was synthesized and purified by following a procedure similar to that described above for 4 using two equivalents of imidazole (4.8 mg, 0.071 mmol) and one equivalent of Mn(TMP)SbF₆ (34.8 mg 0.035 mmol). The final X-ray quality product was obtained via similar approach as 1. Yield after recrystallization: 35.8 mg, 69.8%. ATR-FTIR ν_{Im} (cm⁻¹): 1532(m). Anal. calc’d for C₅₄H₄₄F₆MnN₈O₄Sb•0.5CH₂Cl₂: C, 54.45; H, 3.77; N, 9.32. Found: C, 54.54; H, 3.85; N, 9.65. HRMS-ESI ([M-L]⁺) calc’d for C₅₁H₄₀MnN₆O₄: 855.2486. Found 855.2494. ([M⁺]⁺) calc’d for C₅₄H₄₄MnN₈O₄: 924.2939. Found 924.3071
The compound was synthesized and purified by following a procedure similar to that described above for 4 using two equivalents of imidazole (5.2 mg, 0.076 mmol), one equivalent of Mn(TFP)SbF$_6$ (37.6 mg 0.039 mmol). The final X-ray quality product was obtained via similar approach as 1. Yield after recrystallization: 31.6 mg, 72.6%. ATR-FTIR $\nu_{\text{NH}}$ (cm$^{-1}$): 3382(w), $\nu_{\text{Im}}$ (cm$^{-1}$): 1533(m). Anal. calc’d for C$_{50}$H$_{32}$F$_{10}$MnN$_8$Sb: C, 54.03; H, 2.90; N, 10.08; Found: C, 53.35; H, 2.74; N, 10.72. HRMS-ESI ([M-L]$^+$) calc’d for C$_{47}$H$_{28}$F$_4$MnN$_6$: 807.1687. Found 807.1679. ([M]$^+$) calc’d for C$_{50}$H$_{32}$F$_4$MnN$_8$: 876.2139. Found 876.2271.

7.4 Result and discussion

7.4.1 Synthesis and characterization

The synthesis of complexes 1-13 were achieved via a similar approach reported previously.$^{45}$ The cationic Mn(Por)SbF$_6$ was used as the precursor to react with either one or two equivalents of target axial groups (Scheme 7.1). Desired products are separated after the recrystallization at low temperature ($\sim$-25 $^\circ$C) with the yield of 64.7% $\sim$ 93.6%. One of the characteristic peaks indicating the formation of desired product is the red shift of $\nu_{\text{X=O}}$ ($X = \text{Ti, V or P}$) peaks from their monomeric species to their Ti=O, (1-2), V=O, (3-5) and P=O, (6-7) adducts (Table 7.1), which confirms the binding via oxygen atom. This is also consistent with other oxido bridged species from previous reports.$^{38,39,46}$ The adducts of Im (8-13) show identical signals of the $\nu_{\text{N-H}}$ and the imidazole ring skeletal stretching peaks at $\sim$3400 cm$^{-1}$ and $\sim$1535 cm$^{-1}$, respectively, which are consistent with previous assignments.$^{47,48}$ This confirms the binding of the imidazole group. Interestingly, the ATR-FTIR responses based on the vibrations of the axial groups appear to have stronger intensity (approximately twice) in the bis-axial adduct (2, 5, 7, 10-13)
compared to mono-axial adducts (1, 3-4, 6, 8-10), suggesting a formation of distinct products when the stoichiometry between axial ligands and metalloporphyrin is changed.

Scheme 7.1. Synthesis of mono-axially substituted 1, 3-4, 6, 8-10 and bis-axially substituted 2, 5, 7, 11-13.

<table>
<thead>
<tr>
<th>Table 7.1 ATR-FTIR assignments of $\nu\equiv\equiv O$ for 1-7.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(tmtaa)Ti=O $^{44}$</td>
</tr>
<tr>
<td>$\nu_{Ti=O} (cm^{-1})$</td>
</tr>
<tr>
<td>(tmtaa)V=O $^{49}$</td>
</tr>
<tr>
<td>$\nu_{V=O} (cm^{-1})$</td>
</tr>
<tr>
<td>Ph$_3$PO</td>
</tr>
<tr>
<td>$\nu_{P=O} (cm^{-1})$</td>
</tr>
</tbody>
</table>
The existence of cationic Mn(Por)SbF$_6$ with distinctive mono-axial substituents and bis-axial substituents are further confirmed from their X-ray crystal structures (Figure 7.1, S1-S8). The structures of pentacoordinate species (1, 6, 8-10) all demonstrate a saddle-shaped distortion of the porphyrin plane, with an obvious out-of-plane displacement around 0.174 ~ 0.242 Å (Table 7.2). The structure suggests that metallic oxido (Ti═O or V═O$^{45}$) bridged complexes have relative shorter Mn–O bond lengths of 2.034~2.080 Å, which are consistent with the reports in oxido chromium(III) porphyrin adducts.$^{38,39}$ The M–O bond length of 1 (2.034 Å) is found to be the shortest among all structurally known cationic pentacoordinate Mn(III) porphyrins, which may suggest a strong interaction between proximal ligand and the manganese center. Unlike the previously known bimetallic species containing saddle-inverted tetraazacyclotetradecine ligands (the “wing-down” configuration),$^{38,50}$ the tmtaa ligand in 1 shows “wing-up” configurations. This “wing-up” configuration of 1 matches the recently reported [V═O–Mn(Por)$^+$]$^{45}$ as well. Interestingly, the isomerization of tmtaa ligand can be triggered under a different condition. Attempts to recrystallize 1 at room temperature (~ 20 °C) yield products that have totally different ATR-FTIR response from the ones prepared at lower temperature (< -20 °C). As shown in the Figure 7.S26, the stretching frequency at around ~1500 cm$^{-1}$ may be assigned as the ν$_{C=\equiv N}$ of (tmtaa)Ti═O. When 1 was recrystallized at low temperature, the ν$_{C=\equiv N}$ is found at 1530 cm$^{-1}$, which is consistent with unbounded (tmtaa)Ti═O$^{44}$ (ν$_{C=\equiv N}$ = 1530 cm$^{-1}$), indicating the tmtaa retains the “wing-up” configurations as shown in Figure 7.1A. However, when 1 was prepared at higher temperature, the ν$_{C=\equiv N}$ is found at 1505 cm$^{-1}$. This is in agreement with a structurally known (tmtaa)Ti═O–Cr(Por)Cl$^{39}$ (ν$_{C=\equiv N}$ = 1502 cm$^{-1}$), which has the tmtaa ligand in the “wing-down” configurations. Preliminary X-ray structure (resolution ~ 1.0 Å) was obtained and depicted in Figure 7.S9, confirming the
hypothetically saddle-inverted “wing-down” tmtaa ligand. However, lacking of crystals with appropriate quality and highly disordered solvent molecules prohibits the complete refinement of this structure. Structural and refinement details are attached in SI as a communication purpose.

Although Ph₃PO and imidazole have been extensively utilized as adducts in catalytic reactions, the structures of [Ph₃PO–Mn(Por)]⁺ or [Im–Mn(Por)]⁺ remains unknown. The mono-axially substituted 6 has revealed a rare example of such linkage, showing the Mn–O distance of 2.045 Å and a relative linear P–O–Mn angle of 170.8°. A slightly smaller (0.19 Å) out-of-plane displacement is observed when compared with Ti≡O or V≡O adducts.

Imidazole substituted manganese porphyrin are important molecular models for mimicking enzymatically catalytic reactivity as well. Only bivalent Mn(II) porphyrins ligated with imidazole have been structurally characterized. Structures of 9 and 10 demonstrate first examples of trivalent [Im-Mn(Por)]⁺ adducts, which is closely related to Mn(III) substituted myoglobins that have several biological applications. The saddle distortion of porphyrin planes are observed in 9 and 10 as well with about 0.17 Å out-of-plane displacement. The Mn–N axial bond length of 9 and 10 falls in the range of 2.170–2.185 Å which is noticeably longer than the Mn–O distance of Ti≡O, V≡O and P≡O. The imidazole ring is observed to be perpendicular to the porphyrin plane and the ring aligns well with the N2–Mn–N4 plane. 9 seems to have a slightly larger axial rotation degree of the imidazole ring compared to 10 (12.5° in 9 vs. 5.5° in 10), which might be due to the crystal packing effect. The structure parameters of 9 and 10 match excellently with the structurally known Mn(III) substituted myoglobin, where the M–N bond lengths is 2.22 Å and a 0.18 Å out-of-plane displacement toward the
proximal His93 group is observed. This might suggest similar catalytic reactivity as the biological systems for pentacordinate species 8-10.

**Table 7.2** Summary of structural parameters for Mn(III)Por with mono- and bis axial substituents.

<table>
<thead>
<tr>
<th># (M:L ratio)</th>
<th>Mn–X</th>
<th>Mn–N</th>
<th>Mn–O–X</th>
<th>ΔD&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (1:1)</td>
<td>2.034</td>
<td>2.017</td>
<td>163.7</td>
<td>0.242</td>
</tr>
<tr>
<td>4&lt;sup&gt;a&lt;/sup&gt; (1:1)</td>
<td>2.080</td>
<td>2.007</td>
<td>163.0</td>
<td>0.230</td>
</tr>
<tr>
<td>5 (1:2)</td>
<td>2.251</td>
<td>2.012</td>
<td>158.1</td>
<td>0</td>
</tr>
<tr>
<td>6 (1:1)</td>
<td>2.059</td>
<td>2.006</td>
<td>170.8</td>
<td>0.190</td>
</tr>
<tr>
<td>7 (1:2)</td>
<td>2.162</td>
<td>2.019</td>
<td>171.5</td>
<td>0</td>
</tr>
<tr>
<td>9 (1:1)</td>
<td>2.170</td>
<td>2.007</td>
<td>-</td>
<td>0.174</td>
</tr>
<tr>
<td>12 (1:2)</td>
<td>2.277</td>
<td>2.012</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>10 (1:1)</td>
<td>2.185</td>
<td>2.005</td>
<td>-</td>
<td>0.177</td>
</tr>
<tr>
<td>13 (1:2)</td>
<td>2.262</td>
<td>2.021</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>Mn&lt;sup&gt;III&lt;/sup&gt;Mb(H&lt;sub&gt;2&lt;/sub&gt;O)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2.22</td>
<td>2.04-2.08</td>
<td>-</td>
<td>0.18</td>
</tr>
<tr>
<td>[Mn(TPP)(H&lt;sub&gt;2&lt;/sub&gt;O)]OTf&lt;sup&gt;36&lt;/sup&gt;</td>
<td>2.105</td>
<td>1.994</td>
<td>-</td>
<td>0.19</td>
</tr>
<tr>
<td>[Mn(TPP)(H&lt;sub&gt;2&lt;/sub&gt;O)&lt;sub&gt;2&lt;/sub&gt;ClO&lt;sub&gt;4&lt;/sub&gt;]&lt;sup&gt;36&lt;/sup&gt;</td>
<td>2.271</td>
<td>2.004</td>
<td>-</td>
<td>0</td>
</tr>
</tbody>
</table>

<sup>a</sup> Structural parameters are from previously known system with Mn(TMP)SbF<sub>6</sub>.<sup>45</sup>
<sup>b</sup> Structure is reported with 70% (coordinated) and 30% (uncoordinated) occupancies for proximal H<sub>2</sub>O trans to His93 group.<sup>54</sup>
<sup>c</sup> Out-of-plane displacements were computed based on the distance between the N<sub>4</sub> plane and axially ligated atom.
Figure 7.1 Crystal structures of mono- and bis-axially substituted species, A(1), B(5), C(6), D(7), E(10) and F(13). Thermal ellipsoids were drawn at the 50% probability level. Solvent molecules, hydrogen atoms and anions are omitted for clarity.

In contrast to the mono-axially substituted species, bis-axially substituted 5, 7, 12 and 13 show planar porphyrin with little deformation (Figure 7.2). This result is in contrast to the chromium(III) porphyrin species, where significant distorted porphyrin planes are observed, owing to the larger cationic size of chromium(III). The distances of Mn to proximal atoms appear to be in the range of 2.162 Å to 2.277 Å, which are much longer compared to the mono-
axially substituted analogues. This elongation of M−X bond length in hexacoordinate manganese(III) porphyrin has been observed as well in previously known [Mn(TPP)(H$_2$O)]OTf and [Mn(TPP)(H$_2$O)$_2$]ClO$_4$ complexes (Table 7.2).$^{36}$ This axial elongation effect can be explained by the Jahn-Teller distortion of high spin Mn(III) center.$^{55-57}$ Since the Mn(III) has a high spin d$^4$ electronic configuration with singly occupied z$^2$ orbital, significant splitting of the degenerate set of d(x$^2$-y$^2$) and d(z$^2$) is anticipated when it goes from a pentacoordinate square pyramidal geometry to an hexacoordinate octahedral environment.

One of the major challenge in synthesizing axially substituted porphyrin is to control the ratio of axial ligands. It is known that for iron(III) porphyrin species, mono-axially substituted species are difficult to separate due to the fact that the equilibrium constant of forming hexacoordinate species is larger than forming the pentacoordinate one. However, this is not true for the manganese(III) species. Due to the Jahn-Teller distortion in hexacoordinate environment, bis-axially substituted species may lose one of axial ligands to form the mono-axially substituted specie. Therefore, careful control of the stoichiometry between the metalloporphyrin and axial ligands is important in order to prepare the metalloporphyrin with target modification. This synthetic approach is known to work on chromium porphyrin species as well.$^{39}$

### 7.4.2 Epoxidation of cyclohexene

In order to test the catalytic reactivity as an oxygen atom transfer reagent, compound 1-8 and 11 were applied in the epoxidation reaction of cyclohexene in which iodosylbenzene was used as oxidant. As can be seen in Table 7.3, no conversion is observed when catalyst is absent and no reaction is observed when (tmtaa)Ti═O is used. The addition of Mn(TPP)Cl shows cyclohexene oxide formation of 39.6% yield and 57.6% selectivity, which is consistent with
literature reports.\textsuperscript{1,19} All entries with mono-axial substituents demonstrate superior reactivity (\textbf{1}, 77.8\%; \textbf{3}, 50.5\%; \textbf{4}, 60.1\%; \textbf{6}, 80.9\%; \textbf{8}, 79.2\%) and selectivity (\textbf{1}, 91.9\%; \textbf{3}, 90.1\%; \textbf{4}, 84.4\%; \textbf{6}, 90.9\%; \textbf{8}, 89.4\%) compared to Mn(TPP)Cl. However, bis-axially substituted species show much lower yield (\textbf{2}, 43.6\%; \textbf{5}, 42.8\%; \textbf{7}, 50.2\%; \textbf{11}, 74.7\%) when compared with their pentacoordinate analogues. It has been proposed\textsuperscript{15} that O=Mn\textsuperscript{V}(L/X)TPP species are required in the process of epoxidation reaction. In solution, bis-axially substituted species may reduce the concentration of reactive pentacoordinate intermediate, and thus reduce the catalytic reactivity.

Among the pentacoordinate species, the effectiveness as epoxidation catalysts of V═O species (50.5 ~ 60.1\% epoxide yield) are relatively lower than that in Ti═O, (77.8\%), P═O (80.9\%) or Im (79.2\%). The rate of epoxide formation of different substituents also varies from one to another. This rate is determined qualitatively according to epoxidation yield at 0.5 h, where a trend of Im (77.4\%) > P═O (67.9\%) > Ti═O (49.6\%) > V═O (38.5\% ~ 45.1\%) is found. The axial group with better electron donating group on the seems to increase the effectiveness, as shown in the comparison of tetra methyl substituted omtaa (\textbf{4}) with tmtaa (\textbf{3}), whose epoxide yields are 50.5\% and 60.1\%, respectively. The Ti═O group is believed to have a stronger donating ability than that of V═O according to the shorter Mn−O bond length (Table 7.2). This may explain the improvement for reactivity of \textbf{1} rather than \textbf{3} or \textbf{4}. However, this trend didn’t hold in the case other than Ti═O and V═O species. No direct relationship between reactivity and Mn−X bond length was identified when L is P═O (Mn−O = 2.059 Å) or Im (Mn−N = 2.170~2.185 Å). In contrast, the formation of epoxides is faster in \textbf{6} and \textbf{8}, showing the binding strength of axial interaction in Mn\textsuperscript{III}(L)(Por) may not be correlated to epoxidation reactivity.
Table 7.3 Epoxidation reaction of cyclohexene. Influence of catalyst, reaction time and axial ligand ratio.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst (M:L ratio)</th>
<th>Time(h)</th>
<th>Conversion$^b$</th>
<th>Yield$^b$ (selectivity)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>4</td>
<td>0%</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>(tmtaa)Ti═O</td>
<td>4</td>
<td>0%</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>Mn(TPP)Cl</td>
<td>0.5</td>
<td>36.7%</td>
<td>20.9% (57.1%)</td>
</tr>
<tr>
<td>4</td>
<td>Mn(TPP)Cl</td>
<td>1</td>
<td>49.5%</td>
<td>27.2% (55.4%)</td>
</tr>
<tr>
<td>5</td>
<td>Mn(TPP)Cl</td>
<td>2</td>
<td>68.9%</td>
<td>39.6% (57.6%)</td>
</tr>
<tr>
<td>6</td>
<td>1 (1:1)</td>
<td>0.5</td>
<td>58.4%</td>
<td>49.6% (85.0%)</td>
</tr>
<tr>
<td>7</td>
<td>1 (1:1)</td>
<td>1</td>
<td>77.5%</td>
<td>68.4% (88.2%)</td>
</tr>
<tr>
<td>8</td>
<td>1 (1:1)</td>
<td>2</td>
<td>84.6%</td>
<td>77.8% (91.9%)</td>
</tr>
<tr>
<td>9</td>
<td>2 (1:2)</td>
<td>2</td>
<td>70.5%</td>
<td>43.6% (61.8%)</td>
</tr>
<tr>
<td>10</td>
<td>3 (1:1)</td>
<td>0.5</td>
<td>45.1%</td>
<td>38.4% (85.3%)</td>
</tr>
<tr>
<td>11</td>
<td>3 (1:1)</td>
<td>1</td>
<td>51.1%</td>
<td>46.0% (90.1%)</td>
</tr>
<tr>
<td>12</td>
<td>3 (1:1)</td>
<td>2</td>
<td>56.0%</td>
<td>50.5% (90.1%)</td>
</tr>
<tr>
<td>13</td>
<td>4 (1:1)</td>
<td>0.5</td>
<td>56.3%</td>
<td>45.1% (79.9%)</td>
</tr>
<tr>
<td>14</td>
<td>4 (1:1)</td>
<td>1</td>
<td>65.3%</td>
<td>53.4% (81.6%)</td>
</tr>
<tr>
<td>15</td>
<td>4 (1:1)</td>
<td>2</td>
<td>71.3%</td>
<td>60.1% (84.4%)</td>
</tr>
<tr>
<td>16</td>
<td>5 (1:2)</td>
<td>2</td>
<td>53.9%</td>
<td>42.8% (79.5%)</td>
</tr>
<tr>
<td>17</td>
<td>6 (1:1)</td>
<td>0.5</td>
<td>75.8%</td>
<td>67.9% (89.6%)</td>
</tr>
<tr>
<td>18</td>
<td>6 (1:1)</td>
<td>1</td>
<td>88.5%</td>
<td>79.4% (90.0%)</td>
</tr>
<tr>
<td>19</td>
<td>6 (1:1)</td>
<td>2</td>
<td>89.0%</td>
<td>80.9% (90.9%)</td>
</tr>
<tr>
<td>20</td>
<td>7 (1:2)</td>
<td>2</td>
<td>57.8%</td>
<td>50.2% (87.0%)</td>
</tr>
<tr>
<td>21</td>
<td>8 (1:1)</td>
<td>0.5</td>
<td>85.5%</td>
<td>77.4% (90.6%)</td>
</tr>
<tr>
<td>22</td>
<td>8 (1:1)</td>
<td>1</td>
<td>88.2%</td>
<td>79.1% (89.6%)</td>
</tr>
<tr>
<td>23</td>
<td>8 (1:1)</td>
<td>2</td>
<td>88.6%</td>
<td>79.2% (89.4%)</td>
</tr>
<tr>
<td>24</td>
<td>11 (1:2)</td>
<td>2</td>
<td>79.9%</td>
<td>74.7% (93.5%)</td>
</tr>
</tbody>
</table>

$^a$: The mole ratio for [C]:[S]:[O] is 5:100:200. Reaction was performed anaerobically.

$^b$: Conversion and yield is determined by $^1$H-NMR based on cyclohexene. Cyclohex-2-en-1-one (5~10%) and cyclohex-2-en-1-ol (4~17%) are observed. Concentrations are determined with 10 mM of CH$_2$Cl$_2$ as internal stand.

$^c$: Selectivity is calculated using equation: selectivity = epoxide yield/conversion
It has been proposed that the rate determining step of epoxidation is the formation of Mn(V)=O/alkene adducts instead of subsequent Mn–O bond cleavage,\(^{17,58}\) therefore, stronger binding of axial ligands may facilitate the Mn–O bond cleavage in \textit{trans} position, but will not affect the rate determine step.

It has been shown experimentally that imidazole type substituents are one of the best co-catalysts in Mn or Fe mediated epoxidation reactions.\(^{59}\) This work also shows the higher effectiveness of imidazole over other ligands with oxygen donors. It is worth mentioning that, although conversion rates of oxygen donors are lower than imidazole, such oxido species can still afford high yield and selectivity as well. This may be important when anchoring such catalyst on solid state metallic oxides materials.

The pentacoordinate catalysts still demonstrate reactivity after the complete consumption of oxidant. Additional equivalents of iodosylbenzene are found to increase the conversion olefin, showing approximate 100% epoxide yield (Table 7.S2). The insolubility of iodosylbenzene in dichloromethane may reduce its effectiveness as the oxidant due to the formation of iodobenzene may cover on the surface. However, this can be solved by grounding iodosylbenzene into small particles via ultrasonication. Significant improvement of reaction rates and epoxide yields are observed. (Table 7.S2)

\textbf{7.4.3 Epoxidation of \textit{trans/cis}-β-methylstyrene}

The reactivity towards aryl olefin species is tested using pentacoordinate Mn(TPP)Cl, 1, 4, 6 and 8. All cationic species are found to have faster kinetics and higher yields (63.7% – 94.8% in 0.5 h) compared with Mn(TPP)Cl (22.8%, in 4 h). The order of epoxide yield with different axial ligands is found as Im > Ti–O > P=O >V–O (Table 7.4). Interestingly, 6 shows lower selectivity towards formation of epoxide with significant formation of aldehydes and ketones.
after reaction is completed, while other species demonstrate no significant change of epoxides when reaction reaches completeness. The formation of benzaldehyde and acetaldehyde have been observed previously and can be explained through radical-induced cleavage of dioxetane. However, formation of phenylacetone seems come from two different sources: either a rearrangement product in the process of epoxide formation or the Lewis acid promoted Meinwald rearrangement after the reaction. This effect is also identical for 6 in the case of cis-β-methylstyrene, which will be discussed together.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Time(h)</th>
<th>Conversion (%)</th>
<th>Yield (selectivity)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mn(TPP)Cl</td>
<td>4</td>
<td>23.0%</td>
<td>22.8% (99.1%)</td>
</tr>
<tr>
<td>2</td>
<td>Mn(TPP)Cl</td>
<td>24</td>
<td>77.0%</td>
<td>76.2% (99.0%)</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>0.5</td>
<td>88.3%</td>
<td>87.9% (99.6%)</td>
</tr>
<tr>
<td>4</td>
<td>1&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.5</td>
<td>100.0%</td>
<td>97.2% (97.2%)</td>
</tr>
<tr>
<td>5</td>
<td>4</td>
<td>0.5</td>
<td>65.8%</td>
<td>63.7% (97.2%)</td>
</tr>
<tr>
<td>6</td>
<td>6&lt;sup&gt;e&lt;/sup&gt;</td>
<td>0.5</td>
<td>87.4%</td>
<td>79.8% (91.4%)</td>
</tr>
<tr>
<td>7</td>
<td>6&lt;sup&gt;f&lt;/sup&gt;</td>
<td>24</td>
<td>87.5%</td>
<td>56.9% (65.1%)</td>
</tr>
<tr>
<td>8</td>
<td>6&lt;sup&gt;g&lt;/sup&gt;</td>
<td>144</td>
<td>89.0%</td>
<td>36.8% (41.3%)</td>
</tr>
<tr>
<td>9</td>
<td>8</td>
<td>0.5</td>
<td>97.3%</td>
<td>94.8% (97.5%)</td>
</tr>
</tbody>
</table>

<sup>a</sup>: The ratio of [C]:[S]:[O] is 5:100:200. 5 min ultrasonication is applied to ground iodosobenzene powder. Reaction was performed anaerobically.

<sup>b</sup>: Conversion and yield is determined by <sup>1</sup>H-NMR based on of trans-β-methylstyrene. Concentrations are determined with 5 mM of CH<sub>2</sub>Cl<sub>2</sub> as internal stand.

<sup>c</sup>: Selectivity is calculated using equation: selectivity = epoxide yield/conversion.

<sup>d</sup>: Three equivalents of iodosylbenzene are used.

<sup>e</sup>: Contain approximate 6% phenylacetone, 1% benzaldehyde and 1% acetaldehyde.

<sup>f</sup>: Contain approximate 11% phenylacetone, 9% benzaldehyde and 9% acetaldehyde.

<sup>g</sup>: Contain approximate 18% phenylacetone, 17% benzaldehyde and 17% acetaldehyde.
The improvement of epoxidation reactivity is also observed in the reactions of cis-β-methylstyrene. The cationic species 1, 3, 4, 6 and 8-10 all show higher conversions compared to Mn(TPP)Cl (Table 7.5). In the case of Mn(TPP)Cl, the formation of trans-β-methylstyrene oxide (57.4%) is obtained instead of the desiring cis-β-methylstyrene oxide (33.9 %), showing cis/trans ratio of 0.59. Completely different selectivity is obtained using the cationic species, in which higher yields of cis-β-methylstyrene oxide (43.9% ~ 65.1%) and lower yields of trans-β-methylstyrene oxide (7.5% ~ 23.5 %) are obtained. The electronic substituents on porphyrin 8-10 are found to influence the selectively of the cis/trans ratio, with the highest ratio being observed in electron withdrawing substituted 10. This is consistent with the report by Jabcobsen, where an electron withdrawing group can increase the MnV/MnIV potential and result in higher cis/trans ratio. Although direct measurement of MnV/MnIV was not obtained, potentials of MnIV/MnIII can be measured via cyclic voltammetry (Table 7.S3), which is in agreement with the cis/trans ratio of different electronic substituents on porphyrin. The cis/trans ratio obtained using 6 is the highest in comparison to other species with the same porphyrin ligands, which may in part due to its high MnIV/MnIII potential as well. However, for other species with the same porphyrin substituents, the differences between potential of MnIV/MnIII are mere and significant differences between their cis/trans ratios are still observed. This could suggest the difference of how the cis/trans ratio is related to other factors on axial substituents. The low yield of cis-β-methylstyrene oxide Mn(TPP)Cl is in contrast to a previously known reported manganese porphyrin with bulky subsistuent, where a higher cis/trans ratio is reported. Interestingly, none of our cationic species appears to generate bulk steric hindrance to affect such cis/trans ratio. We believe the cis/trans ratio observed is related to the electronic effect on the axial substituents. Studies have shown tetravalent Mn(IV)═O
may undergo different catalytic routes and affect the cis/trans ratio.\textsuperscript{17} However, such intermediate is known to generate poor steric selectivity\textsuperscript{63} and therefore we rule out the possibility of Mn(IV)═O being the major intermediate. It is worth mentioning that the \textit{in situ} epoxide rearrangement reactions are observed in 6 as well, where the initially formed trans/cis-β-methylstyrene oxide either under isomerization reaction to form phenylacetone and 2-phenylpropanal (Table 7.6) or degrade to form acetaldehyde and benzaldehyde. This is consistent with the observation in trans-β-methylstyrene. Surprisingly, in spite of the lower initial concentration of trans-β-methylstyrene oxide (7.5 % in 0.5 h) compared to the initial concentration of cis-β-methylstyrene oxide (50.4 % in 0.5 h), both epoxides are consumed significantly overtime in \textit{in situ}. This affects the cis/trans ratio significantly (>33 cis/trans in 96 h).

Unlike 6, others show very little change within time and no isomerization to form the carbonyl products. It is known that other Lewis Acids are able to undergo Meiwald rearrangement.\textsuperscript{13,60} The observed epoxide isomerization of 6 may suggest a similar reaction can happen using cationic manganese porphyrins as the Lewis Acid. Interestingly, this effect was significantly influenced by the axial modification. By far, Ph\textsubscript{3}PO group is the only axial ligand of this work that demonstrates such reactivity. We believe this is due to the stabilization of Ph\textsubscript{3}PO in formation the hexacoordinate Mn(III) porphyrin. Previous discussion has revealed that the Jahn-Teller distortion significantly elongates the axial bond length. However, bis-axially Ph\textsubscript{3}PO substituted 7 shows ~0.7 Å shorter in the Mn–X bond length compared to other hexacoordinate species (5, 12-13). As suggested in previous work,\textsuperscript{15,17,58} the formation of hexacoordinate Mn(III) intermediates are involved in the oxidative reaction of alkene which may lead to isomerization products. In additional, such hexacoordinate species are required for
Meiwald rearrangement.\textsuperscript{13,60} Those intermediates could be destabilized due to the elongation of axial ligand owing to Jahn-Teller distortion of high spin Mn(III). However, Ph\textsubscript{3}PO is found to have the capability to form more stable hexacoordinate intermediate and thus promote formation of carbonyl species either during the oxidative reaction or through the subsequent isomerization reaction.

**Table 7.5** Epoxidation reaction of *cis*-β-methylstyrene. Influence of different catalysts.

<table>
<thead>
<tr>
<th>Entry\textsuperscript{a}</th>
<th>Catalyst</th>
<th>Time(h)</th>
<th>Conversion\textsuperscript{a}</th>
<th>cis/trans</th>
<th>trans</th>
<th>Cis</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mn(TPP)Cl</td>
<td>0.5</td>
<td>100%</td>
<td>0.59</td>
<td>57.4%</td>
<td>33.9%</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>0.5</td>
<td>96.1%</td>
<td>3.03</td>
<td>18.3%</td>
<td>55.6%</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>0.5</td>
<td>80.3%</td>
<td>1.83</td>
<td>23.7%</td>
<td>43.9%</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>0.5</td>
<td>87.7%</td>
<td>1.89</td>
<td>23.5%</td>
<td>44.5%</td>
</tr>
<tr>
<td>5</td>
<td>6</td>
<td>0.5</td>
<td>94.4%</td>
<td>6.72</td>
<td>7.5%</td>
<td>50.4%</td>
</tr>
<tr>
<td>6</td>
<td>6\textsuperscript{c}</td>
<td>24</td>
<td>93.3%</td>
<td>8.01</td>
<td>5.5%</td>
<td>43.6%</td>
</tr>
<tr>
<td>7</td>
<td>6\textsuperscript{d}</td>
<td>96</td>
<td>94.1%</td>
<td>&gt;33</td>
<td>&lt;1%</td>
<td>32.8%</td>
</tr>
<tr>
<td>8</td>
<td>8</td>
<td>0.5</td>
<td>100%</td>
<td>5.92</td>
<td>11.0%</td>
<td>65.1%</td>
</tr>
<tr>
<td>9</td>
<td>9</td>
<td>0.5</td>
<td>93.6%</td>
<td>5.48</td>
<td>10.8%</td>
<td>59.2%</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>0.5</td>
<td>100%</td>
<td>7.11</td>
<td>8.5%</td>
<td>60.4%</td>
</tr>
</tbody>
</table>

\textsuperscript{a}: The ratio of [C]:[S]:[O] is 5:100:200. 5 min ultrasonication is applied to ground iodosylbenzene powder. Reaction is performed anaerobically.

\textsuperscript{b}: Conversion and yield is determined by \textsuperscript{1}H-NMR based on *cis*-β-methylstyrene.

\textsuperscript{c}: About ~4% acetaldehyde and ~3% benzaldehyde are found.

\textsuperscript{d}: About ~8% acetaldehyde and ~11% benzaldehyde are found.
### Table 7.6: Epoxidation reaction of cis-β-methylstyrene. Formation of isomerization product

<table>
<thead>
<tr>
<th>Entry&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Catalyst</th>
<th>Time(h)</th>
<th>Conversion&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Ketone&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Aldehyde&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mn(TPP)Cl</td>
<td>0.5</td>
<td>9.7%</td>
<td>9.7%</td>
<td>&lt;1%</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>0.5</td>
<td>24.2%</td>
<td>20.7%</td>
<td>3.5%</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>0.5</td>
<td>28.5%</td>
<td>22.6%</td>
<td>5.9%</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>0.5</td>
<td>27.9%</td>
<td>22.4%</td>
<td>5.5%</td>
</tr>
<tr>
<td>5</td>
<td>6</td>
<td>0.5</td>
<td>39.1%</td>
<td>27.2%</td>
<td>11.9%</td>
</tr>
<tr>
<td>6&lt;sup&gt;c&lt;/sup&gt;</td>
<td>6&lt;sup&gt;c&lt;/sup&gt;</td>
<td>24</td>
<td>39.4%</td>
<td>27.8%</td>
<td>11.6%</td>
</tr>
<tr>
<td>7</td>
<td>6&lt;sup&gt;c&lt;/sup&gt;</td>
<td>96</td>
<td>44.7%</td>
<td>32.0%</td>
<td>12.7%</td>
</tr>
<tr>
<td>8</td>
<td>8</td>
<td>0.5</td>
<td>22.6%</td>
<td>18.9%</td>
<td>3.7%</td>
</tr>
<tr>
<td>9</td>
<td>9</td>
<td>0.5</td>
<td>26.3%</td>
<td>20.5%</td>
<td>5.8%</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>0.5</td>
<td>27.9%</td>
<td>23.1%</td>
<td>4.8%</td>
</tr>
</tbody>
</table>

<sup>a</sup>: The ratio of [C]:[S]:[O] is 5:100:200. 5 min ultrasonication is applied to ground iodosylbenzene powder.

<sup>b</sup>: Conversion is the sum of and ketone (phenylacetone) and aldehyde (2-phenylpropanal). Yield is determined by <sup>1</sup>H-NMR based on cis-β-methylstyrene.

<sup>c</sup>: Acetaldehyde and benzaldehyde are observed as in Table 7.5.

#### 7.5 Conclusion

As a summary, we demonstrate a simple and straightforward synthetic approach to prepare penta- and hexacoordinate manganese(III) porphyrins with targeted axial modifications. X-ray structural characterization have revealed first examples of mono- and bis-axially substituted manganese(III) with titanyl, vanadyl, triphenylphosphine oxide, and imidazole groups. The
effectiveness using such cationic manganese(III) porphyrins as epoxidation catalysts are discussed. Due to the reactive oxidant binding site of pentacoordinate species, superior reactivity is observed over their hexacoordinate species. The enhancement of trans/cis-β-methylstyrene epoxidation are observed showing good to high yield and selectivity. The Ph₃PO substituted species also demonstrates the ability to catalyzed in situ Meinwald-type rearrangement of epoxides, forming carbonyl product.

7.6 Supporting information

X-ray Crystallography Detail

Figure 7.S1. X-ray crystal structure of 1. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms, anion and solvent molecules are omitted for clarity.

A metallic dark black plate-like specimen of C₆₈H₅₄Cl₇F₆MnN₈OSbTi, approximate dimensions 0.562 mm × 0.345 mm × 0.162 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.
A total of 1800 frames were collected. The total exposure time was 11.92 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 356861 reflections to a maximum θ angle of 36.318° (0.60 Å resolution), of which 31595 were independent (average redundancy 11.29, completeness = 100.0 %, Rint = 4.54%, Rsig = 2.65%) and 24086 (76.23%) were greater than 2σ(F^2). The final cell constants of a = 16.5957(5) Å, b = 20.0725(5) Å, c = 19.6188(5) Å, α = 90°, β = 94.4910(10)°, γ = 90°, volume = 6515.3(3) Å^3, are based upon the refinement of the XYZ-centroids of 9407 reflections above 20 σ(I) with 4.562° < 2θ < 72.662°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.8379.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P2_1/n, with Z = 4 for the formula unit, C_{68}H_{54}Cl_{4}F_{6}MnN_{8}OSbTi. The final anisotropic full-matrix least-squares refinement on F^2 with 871 variables converged at R_1 = 3.87 %, for the observed data and wR_2 = 10.48 % for all data. The goodness-of-fit was 1.098. The largest peak in the final difference electron density synthesis was 1.964 e-/Å^3 and the largest hole was -0.642 e-/Å^3 with an RMS deviation of 0.078 e-/Å^3. On the basis of the final model, the calculated density was 1.508 g/cm^3 and F(000), 2984.0 e-.

SQUEEZE of PLATON was applied to deal with disordered solvent. Analysis revealed 413 cubic angstroms of void space and 169 electrons house therein. This approximates to 4 CH_2Cl_2 per unit cell, or 2 per formula unit.
**Figure 7.S2.** X-ray crystal structure of 5. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms, anion and solvent molecules are omitted for clarity.

A black block-like specimen of C_{50}H_{48.01}Cl_{4}F_{3}Mn_{0.5}N_{6}OSb_{0.5}V, approximate dimensions 0.850 mm × 0.566 mm × 0.198 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

A total of 1501 frames were collected. The total exposure time was 11.83 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 170518 reflections to a maximum θ angle of 36.318° (0.60 Å resolution), of which 22685 were independent (average redundancy 7.52, completeness = 99.9 %, Rint = 2.58%, Rsig = 1.63%) and 19796 (87.26%) were greater than 2σ(F^2). The final cell constants of a = 15.8574(5) Å, b = 13.6978(5) Å, c = 22.9511(8) Å, α = 90°, β = 110.090(2)°, γ = 90°, volume = 4681.9(3) Å^3, are based upon the
refinement of the XYZ-centroids of 9610 reflections above 20 σ(I) with 4.848° < 2θ < 73.64°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.8197.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P2_1/n, with Z = 4 for the formula unit, C_{50}H_{48.01}Cl_{3}F_{3}Mn_{0.5}N_{6}OSb_{0.5}V. The final anisotropic full-matrix least-squares refinement on F^2 with 646 variables converged at R_1 = 3.56 %, for the observed data and wR_2 = 8.81 % for all data. The goodness-of-fit was 1.133.

The largest peak in the final difference electron density synthesis was 1.146 e-/Å^3 and the largest hole was -0.678 e-/Å^3 with an RMS deviation of 0.086 e-/Å^3. On the basis of the final model, the calculated density was 1.542 g/cm^3 and F(000), 2216.0 e^-.

Figure 7.S3. X-ray crystal structure of 6. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms, anion and solvent molecules are omitted for clarity.
A metallic dark black needle-like specimen of $\text{C}_{62}\text{H}_{43}\text{F}_6\text{Mn}_4\text{OPSb}$, approximate dimensions $0.756 \text{ mm} \times 0.354 \text{ mm} \times 0.227 \text{ mm}$, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

A total of 626 frames were collected. The total exposure time was 11.97 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 64059 reflections to a maximum $\theta$ angle of $26.732^\circ$ (0.79 Å resolution), of which 11456 were independent (average redundancy 5.62, completeness = 99.7 %, $R_{int} = 4.08\%$, $R_{sig} = 5.07\%$) and 9260 (80.83%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 13.3710(11) \ \text{Å}$, $b = 14.0945(11) \ \text{Å}$, $c = 15.9986(13) \ \text{Å}$, $\alpha = 111.871(3)^\circ$, $\beta = 93.580(4)^\circ$, $\gamma = 101.753(4)^\circ$, volume = $2707.5(4) \ \text{Å}^3$, are based upon the refinement of the XYZ-centroids of 9085 reflections above 20 $\sigma(I)$ with $4.504^\circ < 2\theta < 55.162^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.7924.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P-1$, with $Z = 2$ for the formula unit, $\text{C}_{62}\text{H}_{43}\text{F}_6\text{Mn}_4\text{OPSb}$. The final anisotropic full-matrix least-squares refinement on $F_2$ with 685 variables converged at $R_1 = 5.98\%$, for the observed data and $wR_2 = 15.58\%$ for all data. The goodness-of-fit was 1.081. The largest peak in the final difference electron density synthesis was $1.146 \text{ e/Å}^3$ and the largest hole was $-0.678 \text{ e/Å}^3$ with an RMS deviation of $0.086 \text{ e/Å}^3$. On the basis of the final model, the calculated density was $1.449 \text{ g/cm}^3$ and $F(000), 1192.0 \text{ e}^{-}$. SQUEEZE of PLATON was applied to deal with disordered solvent. Analysis revealed 308 cubic angstroms of void space and 94 electrons house therein. This approximates to 3 $\text{CH}_2\text{Cl}_2$ per unit cell, or 1.5 per formula unit.
A metallic dark black plate-like specimen of $\text{C}_{81}\text{H}_{60}\text{Cl}_2\text{MnN}_4\text{O}_2\text{P}_2\text{Sb}$, approximate dimensions $0.497 \text{ mm} \times 0.433 \text{ mm} \times 0.256 \text{ mm}$, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

A total of 913 frames were collected. The total exposure time was 6.00 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 177170 reflections to a maximum $\theta$ angle of $34.338^\circ$ (0.63 Å resolution), of which 28732 were independent (average redundancy 8.08, completeness = 100.0 %, $R_{\text{int}} = 4.57\%$, $R_{\text{sig}} = 3.23\%$) and 21933 (76.34%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 17.7455(4)$ Å, $b = 18.5936(4)$ Å, $c = 277$
22.1870(5) Å, α = 90°, β = 110.3860(10)°, γ = 90°, volume = 6862.1(3) Å³, are based upon the refinement of the XYZ-centroids of 9757 reflections above 2σ(I) with 5.020° < 2θ < 69.366°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.9003.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P2₁/n, with Z = 4 for the formula unit, C₈₁H₆₀Cl₂F₆MnN₄O₂P₂Sb. The final anisotropic full-matrix least-squares refinement on F² with 902 variables converged at R₁ = 3.64 %, for the observed data and wR² = 9.55 % for all data. The goodness-of-fit was 1.055.The largest peak in the final difference electron density synthesis was 1.471 e⁻/Å³ and the largest hole was -1.237 e⁻/Å³ with an RMS deviation of 0.092 e⁻/Å³. On the basis of the final model, the calculated density was 1.495 g/cm³ and F(000), 3136.0 e⁻.

**Figure 7.S5.** X-ray crystal structure of 9. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms, anion and solvent molecules are omitted for clarity.
A metallic dark block-like specimen of C\textsubscript{53}H\textsubscript{44}Cl\textsubscript{4}F\textsubscript{6}Mn\textsubscript{6}O\textsubscript{4}Sb, approximate dimensions 0.903 mm \times 0.447 mm \times 0.283 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

A total of 1596 frames were collected. The total exposure time was 17.18 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 207716 reflections to a maximum \( \theta \) angle of 36.318° (0.60 Å resolution), of which 25074 were independent (average redundancy 8.28, completeness = 100.0 %, \( R_{\text{int}} = 3.61\% \), \( R_{\text{sig}} = 2.69\% \)) and 19757 (76.34%) were greater than 2\( \sigma(F^2) \). The final cell constants of \( a = 13.4582(3) \) Å, \( b = 14.2885(4) \) Å, \( c = 15.0649(4) \) Å, \( \alpha = 111.2470(10)^{\circ} \), \( \beta = 91.5850(10)^{\circ} \), \( \gamma = 104.7720(10)^{\circ} \), volume = 2587.51(12) Å\textsuperscript{3}, are based upon the refinement of the XYZ-centroids of 9401 reflections above 20 \( \sigma(I) \) with 4.584° < 2\( \theta \) < 74.050°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.9000.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P-1, with \( Z = 2 \) for the formula unit, C\textsubscript{53}H\textsubscript{44}Cl\textsubscript{4}F\textsubscript{6}Mn\textsubscript{6}O\textsubscript{4}Sb. The final anisotropic full-matrix least-squares refinement on \( F^2 \) with 718 variables converged at \( R_1 = 3.97\% \), for the observed data and \( wR_2 = 11.17 \% \) for all data. The goodness-of-fit was 1.131. The largest peak in the final difference electron density synthesis was 1.186 e/Å\textsuperscript{3} and the largest hole was -1.006 e/Å\textsuperscript{3} with an RMS deviation of 0.116 e/Å\textsuperscript{3}. On the basis of the final model, the calculated density was 1.619 g/cm\textsuperscript{3} and F(000), 1268.0 e\textsuperscript{–}. 

279
Figure 7.S6. X-ray crystal structure of 10. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms, anion and solvent molecules are omitted for clarity.

A metallic dark black block-like specimen of C$_{50.5}$H$_{35}$Cl$_7$F$_{10}$MnN$_6$Sb, approximate dimensions 0.420 mm × 0.283 mm × 0.121 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

A total of 1235 frames were collected. The total exposure time was 14.85 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a orthorhombic unit cell yielded a total of 207716 reflections to a maximum θ angle of 36.318° (0.60 Å resolution), of which 25074 were independent (average redundancy 8.28, completeness = 100.0 %, Rint = 3.61%, Rsig = 2.69%) and 19757 (76.34%) were greater than 2σ(F$^2$). The final cell constants of a = 13.4582(3) Å, b = 14.2885(4) Å, c = 15.0649(4) Å, α = 111.2470(10)°, β = 91.5850(10).°, γ = 104.7720(10).°, volume = 2587.51(12) Å$^3$, are based upon the refinement of the XYZ-centroids of 9401 reflections above 20 σ(I) with 4.584° < 2θ < 74.050°. Data were corrected for absorption effects using the multi-
scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.9000.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P-1, with Z = 2 for the formula unit, C$_{50.5}$H$_{35}$Cl$_7$F$_{10}$Mn$_6$Sb. The final anisotropic full-matrix least-squares refinement on F$_2$ with 718 variables converged at R$_1$ = 3.97 %, for the observed data and wR$_2$ = 11.17 % for all data. The goodness-of-fit was 1.131. The largest peak in the final difference electron density synthesis was 1.186 e/Å$^3$ and the largest hole was -1.006 e/Å$^3$ with an RMS deviation of 0.116 e/Å$^3$. On the basis of the final model, the calculated density was 1.619 g/cm$^3$ and F(000), 1268.0 e$^-$.

![Figure 7.S7. X-ray crystal structure of 12. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms, anion and solvent molecules are omitted for clarity.](image)

A metallic dark black block-like specimen of C$_{108}$H$_{88}$F$_{12}$Mn$_2$N$_{16}$O$_8$Sb$_2$, approximate dimensions 0.589 mm $\times$ 0.468 mm $\times$ 0.352 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.
A total of 857 frames were collected. The total exposure time was 15.93 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 183684 reflections to a maximum θ angle of 25.230° (0.83 Å resolution), of which 20669 were independent (average redundancy 8.89, completeness = 100.0 %, Rint = 5.64%, Rsig = 3.00%) and 15442 (74.71%) were greater than 2σ(F²). The final cell constants of a = 25.5259(12) Å, b = 19.8722(8) Å, c = 22.4977(10) Å, α = 90°, β = 97.640(2)°, γ = 90°, volume = 11310.8(9) Å³, are based upon the refinement of the XYZ-centroids of 9679 reflections above 20 σ(I) with 4.684° < 2θ < 51.326°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.8763.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P2₁/C, with Z = 4 for the formula unit, C₁₀₈H₈₈F₁₂Mn₂N₁₆O₈Sb₂. The final anisotropic full-matrix least-squares refinement on F² with 1409 variables converged at R₁ = 7.94 %, for the observed data and wR₂ = 22.86 % for all data. The goodness-of-fit was 1.075. The largest peak in the final difference electron density synthesis was 1.288 e⁻/Å³ and the largest hole was -1.089 e⁻/Å³ with an RMS deviation of 0.141 e⁻/Å³. On the basis of the final model, the calculated density was 1.362 g/cm³ and F(000), 4688.0 e⁻.

SQUEEZE of PLATON was applied to deal with disordered solvent. Analysis revealed 1941 cubic angstroms of void space and 693 electrons house therein. This approximates to 10 CH₂Cl₂ per unit cell, or 2.5 per formula unit.
A metallic dark black plate-like specimen of C$_{52}$H$_{36}$Cl$_4$F$_{10}$MnN$_8$Sb, approximate dimensions 0.518 mm × 0.194 mm × 0.155 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

A total of 825 frames were collected. The total exposure time was 19.42 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 112530 reflections to a maximum θ angle of 27.878° (0.76 Å resolution), of which 12151 were independent (average redundancy 9.26, completeness = 100.0 %, Rint = 3.46%, Rsig = 2.33%) and 9984 (82.17%) were greater than 2σ(F$^2$). The final cell constants of a = 23.0249(7) Å, b = 11.0600(4) Å, c = 21.2454(6) Å, α = 90°, β = 109.8250(10)°, γ = 90°, volume = 5089.6(3) Å$^3$, are based upon the refinement of the XYZ-centroids of 9913 reflections above 20 σ(I) with 4.318° < 2θ < 56.408°.
Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.9315.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P2₁/c, with Z = 4 for the formula unit, C₅₂H₃₆Cl₄F₁₀Mn₈Sb. The final anisotropic full-matrix least-squares refinement on F² with 695 variables converged at R₁ = 4.24 %, for the observed data and wR₂ = 11.47 % for all data. The goodness-of-fit was 1.065. The largest peak in the final difference electron density synthesis was 1.733 e⁻/Å³ and the largest hole was -0.925 e⁻/Å³ with an RMS deviation of 0.100 e⁻/Å³. On the basis of the final model, the calculated density was 1.672 g/cm³ and F(000), 2552.0 e⁻.

**Figure 7.S9.** Preliminary X-ray crystal structure of 1. This is used to compare with the structure obtained at -20 °C (Figure 7.S1). Hydrogen atoms are omitted for clarity. This structure was used as communication purpose due to low resolution.
A metallic black plate-like specimen of $C_{64}F_3MnN_8OSb_{0.5}Ti$, approximate dimensions $0.593 \text{ mm} \times 0.370 \text{ mm} \times 0.285 \text{ mm}$, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

A total of 346 frames were collected. The total exposure time was 11.82 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 59338 reflections to a maximum $\theta$ angle of $20.599^\circ$ (1.01 Å resolution), of which 6968 were independent (average redundancy 8.55, completeness = 99.9 %, $R_{int} = 8.55\%$, $R_{sig} = 5.07\%$) and 5504 (78.99%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 24.809(3) \text{ Å}$, $b = 16.7437(17) \text{ Å}$, $c = 17.198(2) \text{ Å}$, $\alpha = 90^\circ$, $\beta = 106.363 (4)^\circ$, $\gamma = 90^\circ$, volume = 6854.6(16) $\text{Å}^3$ (this is a totally different cell compared with the result of 1 in Figure 7.S1, where $a = 16.5957(5) \text{ Å}$, $b = 20.0725(5) \text{ Å}$, $c = 19.6188(5) \text{ Å}$, $\alpha = 90^\circ$, $\beta = 94.4910(10)^\circ$, $\gamma = 90^\circ$, volume = 6515.3(3) $\text{Å}^3$), are based upon the refinement of the XYZ-centroids of 9859 reflections above 20 $\sigma(I)$ with $4.36^\circ < 2\theta < 40.70^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.5351.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/c$, with $Z = 4$ for the formula unit, $C_{64}F_3MnN_8OSb_{0.5}Ti$. The final anisotropic full-matrix least-squares refinement on $F_2$ with 325 variables converged at $R_1 = 13.19\%$, for the observed data and $wR_2 = 32.03\%$ for all data. The goodness-of-fit was 1.069. The largest peak in the final difference electron density synthesis was $1.26 \text{ e/Å}^3$ and the largest hole was $-1.10 \text{ e/Å}^3$ with an RMS deviation of $0.179 \text{ e/Å}^3$. On the basis of the final model, the calculated density was $1.663 \text{ g/cm}^3$ and $F(000)$, 3496.0 $\text{e}^-$. 

285
<table>
<thead>
<tr>
<th>Identification</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>CaH₂O₂C₂F₆MnN₆O₅SbTi</td>
<td>CaH₂O₂C₂F₆MnO₆Sb</td>
<td>CaH₂O₂C₂F₆MnO₆OPSb</td>
<td>CaH₂O₂C₂F₆Mn₃O₄Sb</td>
<td>CaH₂O₂C₂F₆Mn₃O₄Sb</td>
<td>CaH₂O₂C₂F₆Mn₃O₄Sb</td>
<td>CaH₂O₂C₂F₆Mn₃O₄Sb</td>
<td>CaH₂O₂C₂F₆Mn₃O₄Sb</td>
<td>CaH₂O₂C₂F₆Mn₃O₄Sb</td>
<td>CaH₂O₂C₂F₆Mn₃O₄Sb</td>
<td>CaH₂O₂C₂F₆Mn₃O₄Sb</td>
<td>CaH₂O₂C₂F₆Mn₃O₄Sb</td>
<td>CaH₂O₂C₂F₆Mn₃O₄Sb</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1749.58</td>
<td>1087.03</td>
<td>1181.66</td>
<td>1544.86</td>
<td>1261.43</td>
<td>1340.68</td>
<td>2319.32</td>
<td>1281.38</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature/ K</td>
<td>100.02</td>
<td>100.04</td>
<td>100.01</td>
<td>100.00</td>
<td>99.99</td>
<td>100.00</td>
<td>100.03</td>
<td>99.96</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
<td>monoclinic</td>
<td>monoclinic</td>
<td>triclinic</td>
<td>monoclinic</td>
<td>triclinic</td>
<td>triclinic</td>
<td>monoclinic</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Space group</td>
<td>P2₁/n</td>
<td>P2₁/n</td>
<td>P2₁/n</td>
<td>P2₁/n</td>
<td>P2₁/n</td>
<td>P2₁/n</td>
<td>P2₁/n</td>
<td>P2₁/n</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c/Å</td>
<td>19.6188(5)</td>
<td>22.9511(8)</td>
<td>15.9986(1)</td>
<td>22.1870(5)</td>
<td>15.0649(4)</td>
<td>15.9393(6)</td>
<td>22.4977(10)</td>
<td>21.2454(6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>α/°</td>
<td>90</td>
<td>90</td>
<td>111.87(3)</td>
<td>90</td>
<td>111.2470(10)</td>
<td>116.141(2)</td>
<td>90</td>
<td>90</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>β/°</td>
<td>94.4910(10)</td>
<td>90.090(2)</td>
<td>93.580(4)</td>
<td>110.3860(10)</td>
<td>91.5850(10)</td>
<td>90.336(2)</td>
<td>97.640(2)</td>
<td>109.8250(10)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>γ/°</td>
<td>90</td>
<td>90</td>
<td>101.753(4)</td>
<td>90</td>
<td>104.7720(10)</td>
<td>116.381(2)</td>
<td>90</td>
<td>90</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volume/Å³</td>
<td>6515.3(3)</td>
<td>6681.9(3)</td>
<td>2707.5(4)</td>
<td>6862.1(3)</td>
<td>2587.51(12)</td>
<td>2578.00(17)</td>
<td>11130.8(9)</td>
<td>5089.6(3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
<td>2</td>
<td>4</td>
<td>2</td>
<td>2</td>
<td>4</td>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ρcalc g/cm³</td>
<td>1.508</td>
<td>1.542</td>
<td>1.449</td>
<td>1.495</td>
<td>1.619</td>
<td>1.727</td>
<td>1.362</td>
<td>1.672</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>μ/mm²</td>
<td>0.953</td>
<td>0.909</td>
<td>0.828</td>
<td>0.772</td>
<td>1.047</td>
<td>1.212</td>
<td>0.770</td>
<td>1.072</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F(000)</td>
<td>0.953</td>
<td>2216.0</td>
<td>1192.0</td>
<td>3136.0</td>
<td>1286.0</td>
<td>1330.0</td>
<td>4868.0</td>
<td>2552.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crystal size/mm³</td>
<td>0.562 × 0.345 × 0.162</td>
<td>0.85 × 0.566 × 0.198</td>
<td>0.756 × 0.356 × 0.227</td>
<td>0.497 × 0.433 × 0.296</td>
<td>0.903 × 0.447 × 0.283</td>
<td>0.420 × 0.283 × 0.121</td>
<td>0.589 × 0.468 × 0.155</td>
<td>0.518 × 0.194 × 0.115</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Radiation</td>
<td>MoKα (λ = 0.71073)</td>
<td>MoKα (λ = 0.71073)</td>
<td>MoKα (λ = 0.71073)</td>
<td>MoKα (λ = 0.71073)</td>
<td>MoKα (λ = 0.71073)</td>
<td>MoKα (λ = 0.71073)</td>
<td>MoKα (λ = 0.71073)</td>
<td>MoKα (λ = 0.71073)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2θ range for data collection/°</td>
<td>3.702 to 72.636</td>
<td>3.522 to 72.636</td>
<td>3.212 to 53.464</td>
<td>2.548 to 68.676</td>
<td>2.926 to 72.636</td>
<td>2.94 to 52.044</td>
<td>2.606 to 50.7</td>
<td>1.88 to 55.756</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Index ranges</td>
<td>-19 ≤ h ≤ 27, -33 ≤ k ≤ 33, -32 ≤ l ≤ 32</td>
<td>-26 ≤ h ≤ 26, -22 ≤ k ≤ 22, 35 ≤ l ≤ 38</td>
<td>-16 ≤ h ≤ 16, -17 ≤ k ≤ 17, -20 ≤ l ≤ 20</td>
<td>-28 ≤ h ≤ 24, -29 ≤ k ≤ 29, -34 ≤ l ≤ 35</td>
<td>-22 ≤ h ≤ 22, -23 ≤ k ≤ 23, -25 ≤ l ≤ 25</td>
<td>-17 ≤ h ≤ 17, -18 ≤ k ≤ 18, -19 ≤ l ≤ 19</td>
<td>-30 ≤ h ≤ 29, -23 ≤ k ≤ 23, -27 ≤ l ≤ 25</td>
<td>-30 ≤ h ≤ 22, -14 ≤ k ≤ 14, -21 ≤ l ≤ 27</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Refractions collected</td>
<td>356861</td>
<td>170518</td>
<td>64059</td>
<td>177170</td>
<td>207716</td>
<td>61130</td>
<td>183684</td>
<td>112530</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Independent reflections</td>
<td>31594</td>
<td>22685</td>
<td>28732</td>
<td>25074</td>
<td>10164</td>
<td>206069</td>
<td>12151</td>
<td>200609/84/14</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Data/restraint s/parameters</td>
<td>31594/0/877</td>
<td>22685/0/646</td>
<td>28732/0/902</td>
<td>25074/0/718</td>
<td>10164/0/09</td>
<td>200609/84/14</td>
<td>12151/0/695</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.098</td>
<td>1.133</td>
<td>1.081</td>
<td>1.055</td>
<td>1.131</td>
<td>1.065</td>
<td>1.075</td>
<td>1.065</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Final R indexes [I=2s(I)]</td>
<td>R₁ = 0.0387, wR₁ = 0.0882</td>
<td>R₁ = 0.0336, wR₁ = 0.0834</td>
<td>R₁ = 0.0364, wR₁ = 0.0834</td>
<td>R₁ = 0.0397, wR₁ = 0.0975</td>
<td>R₁ = 0.0261, wR₁ = 0.1772</td>
<td>R₁ = 0.0794, wR₁ = 0.1999</td>
<td>R₁ = 0.0424, wR₁ = 0.1058</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>R₁ = 0.0645, wR₁ = 0.1048</td>
<td>R₁ = 0.0442, wR₁ = 0.0881</td>
<td>R₁ = 0.0618, wR₁ = 0.1117</td>
<td>R₁ = 0.0618, wR₁ = 0.0955</td>
<td>R₁ = 0.0385, wR₁ = 0.1954</td>
<td>R₁ = 0.1089, wR₁ = 0.2286</td>
<td>R₁ = 0.0569, wR₁ = 0.1147</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Largest diff. peak/ hole / e Å⁻³</td>
<td>1.97/0.64</td>
<td>1.15/0.68</td>
<td>1.85/1.32</td>
<td>1.47/1.24</td>
<td>1.19/1.01</td>
<td>1.61/2.09</td>
<td>1.29/1.09</td>
<td>1.73/0.93</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 7.S2. Selective structure parameters for 1 with “wing-up” and “wing-down”) configurations.

<table>
<thead>
<tr>
<th></th>
<th>Mn−X</th>
<th>Mn−N</th>
<th>Mn−O−X</th>
<th>ΔD&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (“wing-up”)</td>
<td>2.034</td>
<td>2.017</td>
<td>163.7</td>
<td>0.242</td>
</tr>
<tr>
<td>1 (“wing-down”)</td>
<td>1.984</td>
<td>1.981</td>
<td>179.4</td>
<td>0.140</td>
</tr>
</tbody>
</table>

*See Figure 7.S1 for structural scheme of “wing-up” configuration and Figure 7.S9 for “wing-down”

<sup>1</sup>H-NMR spectra of representative epoxidation reactions.

Figure 7.S10. Selected <sup>1</sup>H-NMR spectrum of cyclohexene epoxidation.
Figure 7.S11. Selected $^1$H-NMR spectrum of trans-$\beta$-methylstyrene epoxidation.

Figure 7.S12. Selected $^1$H-NMR spectrum of cis-$\beta$-methylstyrene epoxidation.
Solid state ATR-FTIR spectra of 1-13

Figure 7.S13. Solid state ATR-FTIR spectrum of 1.

Figure 7.S14. Solid state ATR-FTIR spectrum of 2.
Figure 7.S15. Solid state ATR-FTIR spectrum of 3.

Figure 7.S16. Solid state ATR-FTIR spectrum of 4.
Figure 7.S17. Solid state ATR-FTIR spectrum of 5.

Figure 7.S18. Solid state ATR-FTIR spectrum of 6.
Figure 7.S19. Solid state ATR-FTIR spectrum of 7.

Figure 7.S20. Solid state ATR-FTIR spectrum of 8.
Figure 7.S21. Solid state ATR-FTIR spectrum of 9.

Figure 7.S22. Solid state ATR-FTIR spectrum of 10.
Figure 7.S23. Solid state ATR-FTIR spectrum of 11.

Figure 7.S24. Solid state ATR-FTIR spectrum of 12.
Figure 7.S25. Solid state ATR-FTIR spectrum of 13.
Figure 7.S26. Solid state ATR-FTIR spectrum of molecules with “wing-up” and “wing-down” geometries.

Detail of electrochemistry

<table>
<thead>
<tr>
<th>Table 7.S4 Cyclic voltammetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Entry</td>
</tr>
<tr>
<td>-------</td>
</tr>
<tr>
<td>Mn(TPP)Cl</td>
</tr>
<tr>
<td>Mn(TPP)SbF₆</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>4</td>
</tr>
<tr>
<td>6</td>
</tr>
<tr>
<td>8</td>
</tr>
<tr>
<td>9</td>
</tr>
<tr>
<td>10</td>
</tr>
</tbody>
</table>
Figure 7.S27. Selected cyclic voltammetry of 6 in dichloromethane solution and referenced to Fc/Fc⁺ = 0 V, with 0.1 M tetra-n-butylammonium hexafluorophosphate (TBAHFP) electrolyte.
### Additional Tables

**Table 7.S3.** Epoxidation reaction of cyclohexene. Influence of oxidant ratio and ultrasonication.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Time (h)</th>
<th>Oxidant (eq.)</th>
<th>Conversion&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Yield&lt;sup&gt;b&lt;/sup&gt; (selectivity)&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>0.5</td>
<td>2</td>
<td>72.9%</td>
<td>71.4% (88.0%)</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>87.8%</td>
<td>84.7% (96.6%)</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>93.4%</td>
<td>86.2% (91.7%)</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>95.6%</td>
<td>89.2% (94.3%)</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>2</td>
<td>2</td>
<td>91.9%</td>
<td>78.2% (85.1%)</td>
</tr>
<tr>
<td>6</td>
<td>3</td>
<td>2</td>
<td>3</td>
<td>91.9%</td>
<td>76.3% (83.0%)</td>
</tr>
<tr>
<td>7</td>
<td>4</td>
<td>2</td>
<td>3</td>
<td>91.9%</td>
<td>78.2% (85.1%)</td>
</tr>
<tr>
<td>8</td>
<td>6</td>
<td>0.5</td>
<td>2</td>
<td>88.9%</td>
<td>79.7% (89.6%)</td>
</tr>
<tr>
<td>9</td>
<td>6</td>
<td>1</td>
<td>2</td>
<td>89.4%</td>
<td>80.2% (89.7%)</td>
</tr>
<tr>
<td>10</td>
<td>6</td>
<td>2</td>
<td>2</td>
<td>89.8%</td>
<td>81.7% (91.0%)</td>
</tr>
<tr>
<td>11</td>
<td>6</td>
<td>2</td>
<td>3</td>
<td>98.1%</td>
<td>92.5% (94.3%)</td>
</tr>
<tr>
<td>12</td>
<td>8</td>
<td>2</td>
<td>3</td>
<td>98.3%</td>
<td>91.9% (93.6%)</td>
</tr>
</tbody>
</table>

<sup>a</sup> The mole ratio for [C]:[S]:[O] is 5:100:200. Reaction was performed anaerobically. 5 min ultrasonication is applied to ground iodosobenzene powder.

<sup>b</sup> Conversion and yield is determined by <sup>1</sup>H-NMR based on cyclohexene. Cyclohex-2-en-1-one (~5%) and cyclohex-2-en-1-ol (~4%) are observed. Concentrations are determined with 10 mM of CH<sub>2</sub>Cl<sub>2</sub> as internal standard.

<sup>c</sup> Selectivity is calculated using equation: selectivity = epoxide yield/conversion.
7.7 Acknowledgement

This work was supported by generous startup funding from North Carolina State University. We acknowledge Prof. Jennifer L. Roizen and Prof. Stefan Franzen for useful discussion. Mass spectra were obtained at the NCSU Department of Chemistry Mass Spectrometry Facility.

7.8 References


