Synthesis and Characterization of Atomic Scale Derivatives and Clusters of Transition Metal Chalcogenides

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By

Tianyang Li

Graduate Program in Chemistry

The Ohio State University

2016

Dissertation Committee:

Dr. Joshua Goldberger, Advisor

Dr. Patrick Woodward

Dr. Claudia Turro
Abstract

Over the recent years, an increasing number of novel crystalline, robust materials that is only single or few atom thick have been created and studied. They are atomic scale derivatives of common solid state structures in which the framework connectivity is terminated with ligands along specific axes. The abrupt termination of the ionic/covalent inorganic framework along a particular direction, gives these materials fundamentally different electronic, optical, thermal, and magnetic properties, which can be manipulated via the design of the organic component. These new materials often exhibit advantageous electronic and optoelectronic behavior, making them viable platforms for applications ranging from light emitting phosphors, to thin film field effect transistors, to photovoltaics.

Using the titanium chalcogenides as model systems, we systematically studied the relative influence of the major synthetic parameters including temperature, ligand structure, and ligand-to-metal stoichiometry on the preparation of the one dimensional atomic scale derivatives of TiS₂. These phases tend to form at high ligand-to-metal ratios and relatively lower temperatures, while the two-dimensional parent lattices are preferred at higher temperature. Although a small change in ligand structure, such as ethylenediamine to propylenediamine will significantly influence the stability of these phases, it will only subtly change the electronic structure. By developing a systematic understanding of the effects of various factors during the synthesis, this work provides a pathway to rationally create new dimensionally reduced materials. Similarly the selenium
analogues of the one dimensional derivatives can also be created. These derivatives exhibit a shift from an indirect to a direct band gap and both the sulfide and the selenide system show a 1.4 eV increment in the band gap energy.

The intercalation of metal cations in 2D layered materials allows for the discovery of unique electronic, magnetic and correlated properties. We demonstrate that reversible Li intercalation is also achievable in the hybrid organic/inorganic dimensionally-reduced 1D van der Waals solid TiS$_2$(ethylenediamine). Upon intercalation, electrons are injected into the lattice as Ti$^{4+}$ is reduced to Ti$^{3+}$ leading to an order of magnitude decrease in electrical resistivity. This reversible intercalation process opens up new opportunities to fine-tune the physical properties in this emerging family of dimensionally-reduced materials.

The vanadium chalcogenide systems are also explored. Reaction temperature, ligand choice and precursor chemistry are studied. The two dimensional organic-intercalated VSe$_2$ inorganic lattices dominate at higher temperature region while the lower temperature region exist various cluster phases, instead of extended lattices as in the titanium chalcogenide systems. For example, we discovered V$_7$S$_8$(en)$_8$Cl$_6$, an electron-deficient corner-sharing dicubane structure, having one unpaired electron per formula. Additionally, in the selenium system, V(en)$_3$Se$_3$ readily forms at low temperatures, and this phase consists of V(en)$_3$$^{2+}$ cations having Se$_3$$^{2-}$ counteranions with no direct V-Se bonding. These clusters represent low-temperature precursor phases towards the two dimensional lattices in these solution phase reactions. The results from this chapter underlines the rich chemistry of the vanadium chalcogenide system and provides a pathway for solution phase
synthesis of intercalated two dimensional VS$_2$ and VSe$_2$ phases as well as other low temperature cluster and precursor phases.

Overall, using titanium and vanadium chalcogenides as model systems, a solution phase synthesis methodology has been develop to create the original two dimensional organic intercalated transition metal chalcogenides, their atomic scale one dimensional chain derivatives and low temperature cluster and precursor phases. The electronic structures and the Li intercalation of the new phases are studied to understand the correlation of properties and structures, leading towards the design and discovery of more useful functional hybrid materials.
Dedication

This document is dedicated to my family.
Acknowledgments

I would like to sincerely thank my advisor Dr. Joshua Goldberger, for his excellent guidance and support throughout the five years of my PhD studies. He encourages a positive and productive atmosphere within the group which makes everyday research more enjoyable. I have learned so much from him not only on scientific research but also the organization and communication skills that will help me throughout my future career. It is my great honor to finish my doctorate study under Dr. Goldberger.

I would also like to thank Dr. Patrick Woodward and Dr. Claudia Turro to serve on my defense committee. Their advice is really valuable to me.

In addition, I want acknowledge all the past and current group member, including Dr. Arijit Ghosh, Sheneve Butler, Dr. Yi-Hsin Liu, Dr. Basant Chitara, Shishi Jiang, Christian Buettner, Zach Baum, Rick Morasse, Nick Cultrara, Maxx Arguilla and Ashley Wallace. You have all been a great help along the way and I treasure the days discussing and doing science with you all. We form a tight bond as researchers and as good friends.

Finally, I want to thank my parents, for their wonderful love throughout my life and also my lovely wife, Qing, for all the support and encouragement over the years that we have met. I could not have done this without you.
Vita

2007-2011 .........................................................B.S. Chemistry, Tsinghua University

2011 to present ................................................Graduate Teaching/Research Assistant,

Department of Chemistry and Biochemistry,

The Ohio State University

Publications


Fields of Study

Major Field: Chemistry
# Table of Contents

Abstract .............................................................................................................................................. ii  
Dedication .......................................................................................................................................... v  
Acknowledgments .............................................................................................................................. vi  
Vita ...................................................................................................................................................... vii  
List of Tables ...................................................................................................................................... xiii  
List of Figures ..................................................................................................................................... xv  
Chapter 1  Introduction .................................................................................................................. 1  
  1.1 Atomic scale derivatives of solid-state materials ................................................................. 1  
  1.2 Synthesis of the atomic scale derivatives .............................................................................. 9  
  1.3 Changes in properties at the atomic scale .......................................................................... 12  
  1.4 Applications of atomic scale derivatives ............................................................................ 19  
  1.5 Chapter Outlines .................................................................................................................... 22  
References .......................................................................................................................................... 23  
Chapter 2  One dimensional chain derivatives of titanium chalcogenides ......................... 37  
  2.1 Introduction ............................................................................................................................ 37  
  2.2 Experimental section ........................................................................................................... 39
2.2.1 Preparation of TiS\(_2\) (en), TiS\(_2\) (pn), TiSe\(_2\) (en) and TiSeO (en) .................. 39

2.2.2 Physical Characterizations ......................................................................................... 41

2.2.3 Density-function-theory calculations ........................................................................... 42

2.3 Crystal structures of the 1D chain derivatives of titanium chalcogenides ........ 43

2.3.1 The structures of TiS\(_2\) (en) and TiS\(_2\) (pn) ......................................................... 43

2.3.2 The structures of TiSe\(_2\) (en) and TiSeO (en) ......................................................... 47

2.4 Synthetic phase diagrams of the titanium sulfide systems .......................................... 53

2.5 Electronic band structures of the 1D sulfide and selenide analogues ..................... 60

2.6 Conclusion ..................................................................................................................... 68

References ........................................................................................................................... 69

Chapter 3 Reversible Li intercalation in the 1D chain derivative TiS\(_2\) (en) ............ 75

3.1 Introduction ..................................................................................................................... 75

3.2 Experimental section ..................................................................................................... 76

3.2.1 Synthesis and purification of TiS\(_2\) (en) ................................................................. 76

3.2.2 Li intercalation and deintercalation .......................................................................... 77

3.2.3 Elemental analysis ...................................................................................................... 78

3.2.4 Powder X-ray diffraction .......................................................................................... 78

3.2.5 Powder neutron diffraction ....................................................................................... 79

3.2.6 X-ray photoelectron spectroscopy (XPS) measurement .......................................... 79
3.2.7 Thin film device fabrication and characterization .......................................................... 80
3.3 Structural changes after Li intercalation ........................................................................ 80
3.4 Probing reversibility by XRD and XPS .......................................................................... 91
3.5 Thin film device and electrical conductivity ................................................................... 94
3.6 Conclusion ....................................................................................................................... 96

References ........................................................................................................................... 97

Chapter 4 Solution phase synthesis of 2D vanadium chalcogenides and low
temperature precursor phases .............................................................................................. 104

4.1 Introduction .................................................................................................................... 104
4.2 \( \text{V}_7\text{S}_8 \) dicubane cluster ............................................................................................ 105
  4.2.1 Experimental section ................................................................................................. 107
  4.2.2 Crystal structure and electron count .......................................................................... 109
  4.2.3 SQUID and EPR measurements ............................................................................. 111
  4.2.4 DFT calculations ..................................................................................................... 113
  4.2.5 Absorption and cyclic voltammetry ......................................................................... 121
4.3 2D vanadium chalcogenides and low temperature precursor phases ......................... 123
  4.3.1 Experimental section ............................................................................................... 124
  4.3.2 Vanadium sulfide system at different temperatures .................................................. 125
  4.3.3 Vanadium selenide system at different temperatures .............................................. 128
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.4 Conclusion</td>
<td>135</td>
</tr>
<tr>
<td>References</td>
<td>136</td>
</tr>
<tr>
<td>Chapter 5 Conclusion</td>
<td>146</td>
</tr>
<tr>
<td>Bibliography</td>
<td>149</td>
</tr>
<tr>
<td>Appendix: Rights and Permissions</td>
<td>184</td>
</tr>
</tbody>
</table>
List of Tables

Table 1.1 A comparison of band gap energies of some parent structures and dimensionally-reduced structures with different polyhedral thickness (ba= butylamine). 13

Table 1.2 A comparison of band gap energies of some parent structures and dimensionally-reduced structures with different organic ligands (ea=ethylamine, pa=propylamine, ha=hexylamine) ..................................................................................................................... 15

Table 2.1 Unit cell parameters of TiS\textsubscript{2}(en) and TiS\textsubscript{2}(pn) ......................................................... 45

Table 2.2 GSAS Rietveld Refinement results for TiS\textsubscript{2}(pn) ............................................................. 46

Table 2.3 Representative bond lengths in TiS\textsubscript{2}(en) and TiS\textsubscript{2}(pn) ......................................................... 47

Table 2.4 Lattice parameters and band gap energy for TiS\textsubscript{2}(en), TiSeO(en) and TiSe\textsubscript{2}(en) .................. 49

Table 3.1 LeBail analysis results of synchrotron XRD patterns of TiS\textsubscript{2}(en) and LiTiS\textsubscript{2}(en) at 100K ................................................................. 83

Table 3.2 Bond lengths and bond valences of TiS\textsubscript{2}(en) and LiTiS\textsubscript{2}(en) ............................................. 84

Table 3.3 GSAS refinement results for neutron diffraction of LiTiS\textsubscript{2}(en) at 2K ............... 86

Table 3.4 GSAS refinement results for neutron diffraction of TiS\textsubscript{2}(en) at 2K ............... 89

Table 3.5 GSAS refinement results for synchrotron XRD patterns of TiS\textsubscript{2}(en) and LiTiS\textsubscript{2}(en) at 100K ................................................................. 90

Table 4.1 Interatomic distances for between V and S atoms in the crystal structure of [V\textsubscript{7}S\textsubscript{8}Cl\textsubscript{2}(en)\textsubscript{8}]Cl\textsubscript{4} and in the [V\textsubscript{7}S\textsubscript{8}Cl\textsubscript{2}(en)\textsubscript{8}]\textsuperscript{4+} cation, optimized within the ROHF and
UHF formalisms with the 6-31G(d,p) basis set and the B3LYP exchange-correlation potential........................................................................................................................................................................114

Table 4.2 MBOs between V and S atoms in the \([\text{V}_7\text{S}_8\text{Cl}_2\text{(en)}_8]^{4+}\) cation, including ROHF and UHF calculations on experimental and ROHF-relaxed structures.................................117

Table 4.3 Comparison of MBOs calculated in this work with those previously reported for metal-metal and metal-sulfur bonds in vanadium sulfide clusters. The V atoms in \([\text{V}_7\text{S}_8\text{Cl}_2\text{(en)}_8]^{4+}\) are categorized into the central \(V_c\) and the six peripheral \(V_p\) atoms....118

Table 4.4 Rietveld refinement results of \(\text{VSe}_3\text{(en)}_3\) .................................................................................................................................132
List of Figures

Figure 1.1 (a) Left: the germanium crystal structure with one (111) plane highlighted in red; right: one layer of the GeH lattice. Atoms: Ge, blue and red; H, black. (b) Left: ZnS lattice (wurtzite) with two (110) planes of tetrahedra highlighted in red; right: Zn$_2$S$_2$(ba) (up) and ZnS(ba) lattices (down) (ba = butylamine). Atoms: Zn, grey and red; S, yellow; C, black; N, blue.

Figure 1.2 (a) Dimensionally-reduced zigzag and linear 1D structures derived from the CdI$_2$ structure type.

Figure 1.3 (a) Left: a perovskite lattice with the general formula AMX$_3$; right: hybrid layered perovskite lattice with the general formula (R-NH$_3$)$_2$MX$_4$. Reproduced with permission from ref 51. Copyright 2013 American Chemical Society. (b) Left: 1D edge-sharing tetrahedral chain highlighted in red in the parent FeSe lattice; right: dimensionally-reduced Fe$_3$Se$_4$(en)$_2$ lattice. Atoms: Fe, red; S, yellow; C, black; N, green.

Figure 1.4 (a) Two-dimensional organic–inorganic Pb iodide perovskites; m is the number of perovskite layers in a 2D structure. (b) Photograph showing material color change with m. (c) Luminescence spectra as a function of m. The m = 3 spectra are similar to the bulk 3D perovskite material. Reprinted with permission from ref. 74. Copyright 2014 American Chemical Society.
Figure 1.5 Measured values for the cross-planar thermal conductivity of unmodified Na-montmorillonite clay and organoclay nanolaminates prepared from varying alkylammonium chain lengths.\textsuperscript{79} Reprinted with permission from ref. 79. Copyright 2013 American Chemical Society.

Figure 1.6 Temperature dependent magnetic susceptibility data of different Fe\textsubscript{3}Se\textsubscript{4}(amine) structures.\textsuperscript{63} Reprinted with permission from ref. 63. Copyright 2015 Royal Society of Chemistry.

Figure 1.7 Room-temperature absorption (a) and emission (b) spectra of [Zn\textsubscript{1.7}Cd\textsubscript{0.3}S\textsubscript{2}(L)] (L=pa, ba, ha, oa). (c) white-light LED aggregates made by coating a thin layer of sample on the surface of a 5 mm reference 360 nm LED: 1) illuminating reference UV LED, 2) the LED in (1) coated with a thin layer of [Zn\textsubscript{1.7}Cd\textsubscript{0.3}S\textsubscript{2}(ha)] before illumination, 3) the LED in (2) illuminating, and 4) [Zn\textsubscript{1.7}Cd\textsubscript{0.3}S\textsubscript{2}(ha)]:0.08%Mn]-coated LED illuminating.\textsuperscript{87} Reproduced with permission from ref 87. Copyright 2012 John Wiley and Sons.

Figure 2.1 Crystal structures of (a) TiS\textsubscript{2}(en) and (b) TiS\textsubscript{2}(pn) projected down the c axis. Ti octahedra are shaded in blue. (c) TiS\textsubscript{2}(en) and (d) TiS\textsubscript{2}(pn) chains along the c axis. (e) en intercalated TiS\textsubscript{2} layers. Atom colors: Ti, blue; S, yellow; N, green; C, black. H atoms are omitted for clarity.

Figure 2.2 Powder x-ray diffraction pattern Rietveld refinement of TiS\textsubscript{2}(pn). Observed data, calculated patterns, and the difference curves are plotted as red, green, and pink, respectively. The 2-Theta reflections are shown in black.
Figure 2.3 View of (a) TiSe$_2$(en) and (b) TiSeO(en) down the c axis. Distorted octahedron of (c) TiSe$_2$(en) and (d) TiSeO(en). (e) TiSeO(en) chain along c axis. ........ 48

Figure 2.4 X-ray fluorescence results of Se/Ti ratio in TiSe$_2$(en) and TiSeO(en). Red line: linear fitting of standard sample mixtures. .......................................................... 48

Figure 2.5 Powder X-ray diffraction patterns of TiSe$_2$(en) (black) and TiSeO(en) (red) 50

Figure 2.6 Rietveld refinement of TiSeO(en). Observed data, calculated patterns, and the difference curves are plotted as black, red, and grey lines, respectively. .................. 51

Figure 2.7 Rietveld refinement of TiSe$_2$(en). Observed data, calculated patterns, and the difference curves are plotted as blue, red, and grey lines, respectively.................. 51

Figure 2.8 Raman spectrum of TiSe$_2$(en) (red), TiSeO(en) (blue) and en-2HCl salt (black). ............................................................................................................. 52

Figure 2.9 Ti-S-Ti bond angle in TiSe$_2$(en) (left), Ti-Se-Ti bond angle in TiSe$_2$(en) (middle) and Ti-O-Ti, Ti-Se-Ti bond angles in TiSeO(en) (right). ......................... 53

Figure 2.10 (a) Synthetic phase space diagram of TiS$_2$(en) system. Red, intercalated TiS$_2$; orange, mixed phases; green, TiS$_2$(en); blue, amorphous. (b) Representative powder X-ray diffraction patterns of each phase. ................................................................. 54

Figure 2.11 (a) Powder X-ray diffraction patterns of products obtained via varying (en): Ti ratio; (i. 30:1, ii. 20:1, iii. 10:1). (b) Powder X-ray diffraction patterns of products obtained via varying temperature; (i. 220°C, ii. 180°C, iii. 140°C, iv. 100°C). en: Ti ratio 20:1. ............................................................................................................. 55
Figure 2.12 (a) Synthetic phase space diagram of TiS$_2$(pn) system. Red, intercalated TiS$_2$; orange, mixed phases; green, TiS$_2$(pn); blue, amorphous. (b) Representative powder X-ray diffraction patterns of each phase.

Figure 2.13 1D TiS$_2$(en) XRD patterns before (black) and after (red) annealed with additional one equivalent of en at 200 °C for 1d.

Figure 2.14 2D intercalated TiS$_2$ XRD patterns before (black) and after (red) annealed with additional 20 equivalents of en at 200 °C for 1d. The starred peak is from the aluminum holder.

Figure 2.15 (a) Diffuse reflectance spectra of both TiS$_2$(en) and TiS$_2$(pn). (b) Calculated band structure of TiS$_2$(en). (c) Partial density of states of Ti 3d (black) and S 3p (red) for TiS$_2$(en). (d) Calculated band structure of TiS$_2$(pn). (e) Partial density of states of Ti 3d (black) and S 3p (red) for TiS$_2$(pn).

Figure 2.16 Partial density of states of (a) TiS$_2$(en) and (b) TiS$_2$(pn) showing Ti, S and N contributions.

Figure 2.17 (a) DRA absorption spectra of TiSe$_2$(en), TiSeO(en) and TiS$_2$(en). (b) Absorption (black) and NIR photoluminescence (red) of TiSe$_2$(en).

Figure 2.18 (a) Local electronic band structure for TiSe$_2$(en). (b) Partial density of states, where s (blue), p (orange), and d (red) orbital contributions are summed (black). (c) Band structure illustrations of TiSe$_2$, TiSe$_2$(en) and TiSeO(en).

Figure 2.19 Photoluminescence comparison at 77K and room temperature.

Figure 2.20 Calculated electronic partial densities of states (PDOS) of Ti, N and Se in TiSe$_2$(en) at room temperature.
Figure 3.1 (a) Crystal structures of TiS$_2$(en) (left) and LiTiS$_2$(en) (right) projected down the $c$ axis. (b)(c) X-ray diffraction patterns of TiS$_2$(en)(black), Li$_{0.66}$TiS$_2$(en)(red) and LiTiS$_2$(en). (d) Changes of unit cell parameter ($a$: black, $c$: red) with respect to Li/Ti ratio. (e) Crystal structures showing two adjacent 1D chains along $c$ axis with intercalated Li atoms positions determined from neutron diffraction refinements. Atom colors: Ti, red; S, yellow; N, green; C, black. H atoms have been omitted for clarity. 

Figure 3.2 Williamson-Hall plot of Li$_{0.66}$TiS$_2$(en) and LiTiS$_2$(en) using TiS$_2$(en) as standard.

Figure 3.3 Inter-chain expansion after Li intercalation.

Figure 3.4 TOF Neutron diffraction pattern Rietveld refinement of LiTiS$_2$(en) at 2K.

Figure 3.5 TOF Neutron diffraction pattern Rietveld refinement of TiS$_2$(en) at 2K.

Figure 3.6 Synchrotron XRD Rietveld refinement of TiS$_2$(en) at 100K.

Figure 3.7 Synchrotron XRD Rietveld refinement of LiTiS$_2$(en) at 100K.

Figure 3.8 (a) shift of peaks in the X-ray diffraction patterns. (b) changes of binding energy of Ti during reversible Li intercalation. (c) changes of Li peaks during reversible Li intercalation. Black: TiS$_2$(en), green: Li intercalated TiS$_2$(en), blue: deintercalated TiS$_2$(en).

Figure 3.9 XPS survey spectra of TiS$_2$(en).

Figure 3.10 XPS survey spectra of Li intercalated TiS$_2$(en).

Figure 3.11 XPS survey spectra of deintercalated LiTiS$_2$(en).

Figure 3.12 (a) Simplified illustration of the thin film device (not drawn to scale). (b) Optical microscope image of one TiS$_2$(en) thin film device; insert: electron scanning.
microscope image of two contacts on the thin film. (c) IV curves of TiS$_2$(en) and LiTiS$_2$(en) in dark and Ar atmosphere. (d) IV curves of LiTiS$_2$(en) at different temperature; insert: resistivity vs. temperature plot.

Figure 4.1 (a) V$_7$S$_8$ core of the dicubane cluster with V-S bond lengths labeled. (b) V$_7$S$_8$Cl$_2$(en)$_8^{4+}$ cluster neglecting H and Cl$^-$ counterions. Color: V, red; S, yellow; Cl, green; C, black; N, blue.

Figure 4.2 (a) Magnetic susceptibility plot and Curie-Weiss fit of the zero-field-cool data. (b) EPR spectrum of the cluster in NMF.

Figure 4.3 Energy level (right) and Molecular orbital isosurfaces (left) for the V$_7$S$_8$Cl$_2$(en)$_8^{4+}$ cation from spin-unrestricted hybrid Hartree Fock/Density Functional Theory calculations (95% probability isosurfaces). The SOMO is outlined in blue and features localization at the central vanadium atom.

Figure 4.4 Zoomed in Molecular orbital isosurfaces for the V$_7$S$_8$Cl$_2$(en)$_8^{4+}$ cation from spin-unrestricted hybrid Hartree Fock/Density Functional Theory calculations (95% probability isosurfaces) for the 7 highest $\alpha$-spin SOMOs.

Figure 4.5 Molecular orbital diagram of the [V$_7$S$_8$Cl$_2$(en)$_8$]$^{4+}$ from ROHF/DFT (left) and UHF/DFT (right).

Figure 4.6 (a) Extinction coefficient vs. wavelength plot calculated from the absorption spectrum in NMF. (b) Cyclic voltammetry plot of the dicubane cluster solution in NMF, showing 1 reduction and 4 oxidation waves. The open circuit voltage occurs at -0.35 V.
Figure 4.7 XRD patterns of products from VCl$_4$ and S powder reactions in en at different temperatures. ................................................................. 126

Figure 4.8 XRD patterns of products from VCl$_4$ and S powder reactions in pn at different temperatures. ................................................................. 127

Figure 4.9 XRD patterns of products from VCl$_4$ and S powder reactions in oo at different temperatures. ................................................................. 128

Figure 4.10 XRD patterns of products from VCl$_4$ and Se powder reactions in en at different temperatures. ................................................................. 129

Figure 4.11 Crystal structure of the low-temperature precursor phase VSe$_3$(en)$_3$. ....... 130

Figure 4.12 Rietveld refinement of VSe$_3$(en)$_3$ lab X-ray powder pattern. .................. 131

Figure 4.13 ZFC plot of VSe$_3$(en)$_3$ and the Curie-Weiss fit. ................................. 132

Figure 4.14 XRD patterns of products from VCl$_4$ and Se and NaBH$_4$ reactions in en at different temperatures. Starred peaks are from impurities.................................. 134
Chapter 1 Introduction

1.1 Atomic scale derivatives of solid-state materials

Since the 1980’s, one of the most extensively studied concepts in materials research has been that new properties and phenomena emerge when solid state materials have one or more dimensions constrained to the nanoscale (<100 nm). It has become quite clear that the electronic, optical, and thermal properties can be dramatically influenced by the length scale, and this concept has opened up novel frontiers of research, such as plasmonics and photonics. As a result of these changes, these nanoscale materials have attracted great interest as ideal building blocks for next generation energy harvesting, sensing, and electronic materials.

While most of these studies have focused on materials that are on the scale of several nanometers and larger, there is an emerging body of work suggesting that the framework connectivity of atoms for any crystalline solid can be terminated along specific axes to create stable, crystalline materials comprised of single- or few-atom thick fragments. The properties of these “dimensionally-reduced” systems are significantly different than even their nanoscale counterparts, and can be dramatically influenced by their surface-terminating ligands and their immediate environment. Entirely unprecedented phenomena can manifest within 1-2 unit cells of a material whose electronic structure is “just right”.

---

such as the ultra-high mobility Fermi-Dirac physics of single-layer graphene\textsuperscript{29-30}, the generation of 2D topological insulators in thin layers of HgTe\textsuperscript{31-32}, and even 2D superconductivity at the interface between LaAlO\textsubscript{3} and SrTiO\textsubscript{3}\textsuperscript{33}. In the past 10 years, methods to characterize and manipulate the properties of single-atom thick materials have been pioneered as a result of the intense interest in low-dimensional materials\textsuperscript{10, 34-38}. Extending this understanding into this emerging class of solid-state materials at the atomic scale will no doubt have broad implications in energy, electronics, and catalysis.

This concept of “dimensional reduction” has been around for some time, and initially was employed to rationalize the changes in polyhedral connectivity of an ionic lattice upon the incorporation of a specific stoichiometry of salt\textsuperscript{25}. For example, in silicates, adding additional stoichiometric equivalents of Na\textsubscript{2}O to the SiO\textsubscript{2} lattice, disrupts the 3D connectivity of corner-sharing Si-O tetrahedra, to produce 2D sheet structures in Na\textsubscript{2}Si\textsubscript{2}O\textsubscript{5} or 1D chains of tetrahedra in Na\textsubscript{2}SiO\textsubscript{3}\textsuperscript{39}. Since the metal and anion oxidation states do not change, the polyhedral geometry is preserved.

Only recently have organic ligands been utilized to disrupt the framework connectivity of an inorganic lattice, giving rise to numerous advantages. The rich structural diversity of organic ligands opens up the potential to tune the dimensionally-reduced framework structure with differences in binding type (i.e. cis- vs. trans-binding), and ligand structure. Furthermore, the use of organic ligands more effectively insulates the inorganic framework than via small cations and anions, leading to much greater changes in properties. Finally, the ability to create high-aspect ratio inorganic materials with precisely defined chemical linkages to functional organic components can facilitate their integration into hybrid
organic/inorganic devices, either as the active material itself, or exfoliated and reincorporated into composites.

**Figure 1.1** (a) Left: the germanium crystal structure with one (111) plane highlighted in red; right: one layer of the GeH lattice\(^{40}\). Atoms: Ge, blue and red; H, black. (b) Left: ZnS lattice (wurtzite) with two (110) planes of tetrahedra highlighted in red; right: Zn\(_2\)S\(_2\)(ba) (up) and ZnS(ba) lattices (down) (\(ba = \text{butylamine}\))\(^{19}\). Atoms: Zn, grey and red; S, yellow; C, black; N, blue.\(^{41}\)

In these ligand-terminated atomic-scale derivatives of solid-state lattices, the framework connectivity of the original parent lattice is preserved along specific lattice
planes or 1D directions. Depending on the crystal chemistry of the original lattice, these inorganic fragments can be terminated with covalent functional groups such as hydrogen or methyl groups, neutral Lewis base ligands such as amines, or organic ions to counterbalance the charges such as organoammonium cations. These atomic-scale derivatives will have specific metal-to-anion-to-ligand stoichiometries depending on the thickness of the inorganic fragment, and the denticity of the ligand. Here, we highlight numerous examples of materials derived from prevalent solid-state crystal structure types.

The diamond lattice is the most common structure type for the group IVA elemental semiconductors, including silicon, germanium, and α-tin. In this structure type, each atom is sp\(^3\)-hybridized and tetrahedrally bonded to 4 neighboring atoms. The lattice can also be viewed as connected layers of puckered, honeycomb (111) planes of atoms (Figure 1.1(a)). In the group IVA graphane analogues, such as germanane (GeH)\(^4\), these (111) layers of atoms are disconnected from one another and surface-ligand terminated such that every Ge atom has 3 bonds to neighboring Ge atoms and a fourth bond to a hydrogen atom.

The wurtzite and sphalerite lattice types are the most common structure type for III-V and II-VI semiconductors. These crystal structures are comprised of 3D networks of corner-sharing metal-anion tetrahedra that are either hexagonally close packed (wurtzite) or cubic close packed (sphalerite). Jing Li et al. has discovered a large library of crystalline amine-terminated 2D derivatives of the wurtzite lattice having the general formula, \(\text{M}_n\text{X}_n\text{L}_y\) (\(M=Mn, Zn, Cd; X=S, Se, Te; L=\text{mono-}, \text{di-amine}; n=1,2; y=0.5, 1\))\(^{19,23,42}\). These materials correspond to single or double-tetrahedral thick 2D (110) planes of tetrahedra extracted from wurtzite(Figure 1.1(b)). In the single tetrahedral thick derivative
(stoichiometry MXL, where L is a mono-amine) each metal is bonded to three chalcogenide atoms and a terminal amine ligand to form a tetrahedron. Each metal tetrahedron is linked in corner-sharing fashion to 6 neighboring tetrahedron through the chalcogenide atom. The double-tetrahedral thick derivatives (MXL0.5, where L = mono-amine) can be visualized as two (110) planes of corner-sharing tetrahedron extracted from wurtzite, with the top and bottom surfaces having the same ligand terminated surfaces.

Figure 1.2 (a) Dimensionally-reduced zigzag and linear 1D structures derived from the CdI₂ structure type.⁴³-⁴⁵
The CdI$_2$ structure type is the most prevalent crystal structure for metal dihalides, and early transition metal dichalcogenides. This is one of the most widely studied classes of materials, as the transition metal dichalcogenides exhibit fascinating correlated electronic phenomena such as charge density waves and superconductivity, and are promising in applications including catalysis, battery electrodes, optoelectronics, and field effect transistors. The structure is comprised of layers of metal anion octahedra that share edges with six neighbors. These layers are held together via van der Waals forces (Figure 1.2). This edge-sharing octahedral network can be terminated with ligands within each 2D plane of octahedra to produce 1D edge-sharing ribbons that can be either linear or zigzag, and single, double, or multiple octahedra in thickness. In general, linear chains form when ligands bond in *trans*-binding configurations and zigzag chains form when ligands bond in *cis*-binding configurations. Additionally, ribbons that feature larger polyhedral thicknesses will have lower ligand-to-metal stoichiometries. For example, CdBr$_2$(DMSO) (DMSO = dimethylsulfoxide) consists of double-octahedral thick zigzag chains of CdBr$_2$, in which the edge CdBr$_2$ octahedron are coordinated to two DMSO molecules in *cis* coordination. Since half of the Cd-Br octahedron do not have ligands bound to them, the stoichiometry of this double octahedral thick chains corresponds to one binding ligand per octahedron. The linear double-octahedral derivative CdCl$_2$(imidazole) features the same overall stoichiometry, with each Cd-Cl octahedra bound to one imidazole ligand.
Figure 1.3 (a) Left: a perovskite lattice with the general formula AMX$_3$; right: hybrid layered perovskite lattice with the general formula (R-NH$_3$)$_2$MX$_4$. Reproduced with permission from ref 51. Copyright 2013 American Chemical Society. (b) Left: 1D edge-sharing tetrahedral chain highlighted in red in the parent FeSe lattice; right: dimensionally-reduced Fe$_3$Se$_4$(en)$_2$ lattice$^{22}$. Atoms: Fe, red; S, yellow; C, black; N, green.

Unlike the systems discussed above in which neutral, covalently bound ligands terminate the surface of the lattice, there are examples of structures in which space filling
cations are replaced with charged organic species to create atomic-scale frameworks. The well-known perovskite lattice has a general formula of AMX₃, where typically A is a larger cation, M is a smaller cation and X is an anion. The perovskite structure is composed of corner-sharing networks of MX₆ octahedra with the larger A-site cations occupying the central 12-coordinate cuboctahedral pockets. The size of the A cation plays an important role in determining the shape of the lattice. Too big or too small of a cation can cause distortion and tilting of the corner-sharing MX₆ octahedral framework, transforming the cubic lattice into lower symmetry space groups. When the A cation is replaced with a large organic cation, very often the 3D connected lattice cannot form and instead forms 2D slabs of corner-sharing octahedra with the organic cations in between the layers (Figure 1.3 (a)). Many hybrid organic-inorganic perovskites with alkylammonium cations fall into this category. The simplest form contains ligand-terminated isolated layers of anionic corner-sharing MX₆ octahedra (M is a divalent metal, such as Sn²⁺ and Pb²⁺, and X is a halide, L = alkyl monoammonium cation) having the stoichiometry of L₂MX₄. Bilayers of cationic organic molecules are ionically associated with the inorganic sheets through the ammonium groups while the alkyl tails extend into the van der Waals gap. Double-, and triple-octahedral thick perovskite lattices have been created and feature ligand-to-metal stoichiometries of 1:1 and 2:3, respectively. Furthermore, by using organic cations with different shapes, dimensionally-reduced frameworks corresponding to the (111), (110), and (100) planes of the original perovskite lattice can be prepared. A wide array of functional organic cations has been used, including chromophores, oligothiophene derivatives, or photopolymerizable butadiene derivatives. The diverse pool of potential
organic cations enables the creation of perovskite frameworks with different tilting and polyhedral connectivity.

As a final example, the 2D FeSe lattice structure type has attracted considerable recent interest, due to the emergence of high temperature superconductivity found in these phases and the closely related 122 structure type\textsuperscript{60-62}. These materials can be thought of as 2D networks of edge-sharing tetrahedra. Kovnir \textit{et al.} created several 1D derivatives of the 2D FeSe lattice. These 1D derivatives have the general formula of $\text{Fe}_3\text{Se}_4\text{L}_x$ where $\text{L}$ is $\text{en}$, diethylenetriamine ($\text{dien}$) and tris(2-aminoethyl)amine ($\text{tren}$)$^{63}$ and possess 1D chains of edge-sharing anionic Fe-Se tetrahedron with octahedral cationic Fe-amine complexes positioned in between the chains. The oxidation state of the Fe atoms in the FeSe$_2$ chains is 3+ and the Fe-amine complexes are 2+. This makes the chains negatively charged while the Fe-amine complex has a positive charge and produces a neutral lattice.

1.2 Synthesis of the atomic scale derivatives

Unlike the solution-phase growth of colloidal nanocrystals\textsuperscript{64-68}, the synthesis of dimensionally reduced solids is still in its infancy. Although for a given lattice framework, one can easily envision the existence of different ligand-terminated dimensionally reduced structures, the targeted synthesis of a specific atomic-scale framework remains elusive. Here, we describe our current understanding of the general synthetic pathways as well as detailed approaches of creating classes of materials, emphasizing the influence of several important factors during the synthesis.
The preparation of dimensionally reduced structures typically relies on two pathways: 1. The kinetically-controlled, topotactic transformation of closely related frameworks; 2. the thermodynamically-controlled, nucleation and crystal growth of a ligand-terminated framework from molecular precursors. The kinetically-controlled pathway requires the initial formation of an intermediate crystalline lattice that incorporates the framework of interest (i.e. a plane of germanium atoms in a honeycomb arrangement), but is reactive enough to form a ligand-terminated product. The thermodynamically-controlled pathway often employs solution-phase chemistries similar to the synthesis of the parent lattice itself, however, the growth of the parent framework is suppressed along specific directions by the presence of ligands that strongly bind to the metal site of the growing lattice. To create the atomic-scale derivatives, it is essential that these ligands bind strongly to the metal under the conditions of synthesis, otherwise, the ligand dissociation will promote inorganic crystal growth along all directions of the lattice and ultimately form nanosized materials.

The synthesis of the group IV graphane analogues has been accomplished by the first pathway, via the topotactic transformation of precursor Zintl phases. Zintl phases are solid-state lattices that are comprised of a network of anionic homonuclear or heteronuclear polyatomic clusters of group 13, 14, 15, or 16 elements, whose charge is counterbalanced with alkali, or alkaline earth elements. In the CaGe$_2$ Zintl phase, Ge$^-$ anions exist in single-atom thick, $sp^3$-hybridized, puckered honeycomb geometries, similar to (111) planes of crystalline Ge, and are separated by layers of Ca$^{2+}$ ions. Upon reaction with concentrated aqueous HCl, the Ca$^{2+}$ cations are removed via the formation of CaCl$_2$, while a coordinating –H ligand is added to each Ge atom, preserving the layered $sp^3$ framework$^{40}$. Similarly,
the Ge layer can be methyl terminated by reacting the Zintl phase with a methylating reagent such as CH$_3$I, which also produces a soluble CaI$_2$ byproduct$^{69}$. These kinetically-controlled pathways often require reactions to occur at low temperatures to minimize decomposition into a more thermodynamically stable product.

The synthesis of many of the dimensionally reduced zinc blende/wurtzite lattices, 2D transition metal chalcogenide lattices and hybrid perovskite frameworks is accomplished via the thermodynamically-controlled pathway.$^{18-21, 23, 42, 55-56}$ Typically, metal and anion precursors having the same oxidation state as the target product are reacted solvothermally in the presence of strongly binding ligands. Metal halides or metal nitrates are usually used as the metal sources. To create the chalcogen precursors with the -2 oxidation state, elemental chalcogens are first reacted with amines first to form H$_2$X before reacting with metal precursors$^{70}$. These sacrificial amines also often serve the role as the same strongly binding ligands that coordinate to the metal. In other cases, neutral metal and chalcogen powders are used as precursors to directly react with amines to create dimensionally reduced FeSe lattices.$^{61, 63}$

Still, we are only at the beginning of our understanding on how to rationally create a specific atomic-scale framework from a particular crystalline material. Very often, the initial discovery of a novel phase is serendipitous. The systematically exploration of different chemistries, different closely related ligands, and different synthetic approaches is often necessary to access structures having different polyhedral connectivities and thicknesses. The general synthetic principles described here lay the foundation for the targeted synthesis of atomic-scale phases.
1.3 Changes in properties at the atomic scale

Reducing the framework of a solid-state lattice to a single polyhedral thickness will produce significant changes in the physical properties of a material. Not only are these changes due to the reduction of the inorganic framework itself, but in some systems, the properties can be manipulated due to the contribution of the organic components. Here we give a brief overview on how the electronic, optical, magnetic and thermal properties in these atomic-scale lattices change compared to the original framework, and how they can be tuned with different ligands.

The electronic structure of atomic-scale derivatives can be completely different compared to the parent framework. First, it is a well-appreciated phenomenon that decreasing the size of a semiconducting material results in a significant increase in band gap as a result of quantum confinement effects\textsuperscript{71-73}. These molecular scale materials represent the extreme case of confinement. Many single polyhedral thick derivatives of semiconductors can have band gaps that are increased by 1-2 eV depending on the material system (Table 1.1)\textsuperscript{19-21}. The band gaps of double-polyhedral thick derivatives can increase by 0.6-1.2 eV. The hybrid perovskites also exhibit this trend of increasing band gap with decreasing inorganic layer thickness, as is evident by the blue shift of the band edge photoluminescence (Figure 1.4)\textsuperscript{74}. Additionally, transitions from indirect to direct band gap can also occur, such as comparing TiS\textsubscript{2} to TiS\textsubscript{2}(en).
Table 1.1 A comparison of band gap energies of some parent structures and dimensionally-reduced structures with different polyhedral thickness (\(ba=\) butylamine).

<table>
<thead>
<tr>
<th>Parent Structures</th>
<th>Band Gap (eV)</th>
<th>Direct / Indirect</th>
<th>Dimensionally Reduced Structures</th>
<th>Band Gap (eV)</th>
<th>Direct / Indirect</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiS(_2)</td>
<td>0.3(^{75})</td>
<td>Indirect</td>
<td>TiS(_2)(en)</td>
<td>1.7(^{20})</td>
<td>Direct</td>
</tr>
<tr>
<td>TiSe(_2)</td>
<td>-0.2(^{76}) (semimetal)</td>
<td>Indirect</td>
<td>TiSe(_2)(en)</td>
<td>1.2(^{21})</td>
<td>Direct</td>
</tr>
<tr>
<td>ZnSe</td>
<td>2.5(^{19})</td>
<td>Direct</td>
<td>ZnSe((ba))</td>
<td>4.1(^{19,77})</td>
<td>Direct</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Zn(_2)Se(_2)(ba)</td>
<td>3.5(^{19})</td>
<td>Direct</td>
</tr>
<tr>
<td>CdS</td>
<td>2.3(^{19})</td>
<td>Direct</td>
<td>CdS((pn))(_{0.5})</td>
<td>4.0(^{19})</td>
<td>Direct</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cd(_2)S(_2)(pn)</td>
<td>2.9(^{19})</td>
<td>Direct</td>
</tr>
</tbody>
</table>
Figure 1.4 (a) Two-dimensional organic–inorganic Pb iodide perovskites; m is the number of perovskite layers in a 2D structure. (b) Photograph showing material color change with m. (c) Luminescence spectra as a function of m. The m = 3 spectra are similar to the bulk 3D perovskite material. Reprinted with permission from ref. 74. Copyright 2014 American Chemical Society.
Table 1.2 A comparison of band gap energies of some parent structures and dimensionally-reduced structures with different organic ligands (ea=ethylamine, pa=propylamine, ha=hexylamine)

<table>
<thead>
<tr>
<th>Parent Structure</th>
<th>Band Gap (eV)</th>
<th>Dimensionally Reduced Structure</th>
<th>Band Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiS$_2$</td>
<td>0.3$^{75}$</td>
<td>TiS$_2$(ea)</td>
<td>1.71$^{20}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TiS$_2$(pn)</td>
<td>1.75$^{78}$</td>
</tr>
<tr>
<td>ZnS</td>
<td>3.5$^{19}$</td>
<td>Zn$_2$S$_2$(ea)</td>
<td>4.0$^{19}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zn$_2$S$_2$(pa)</td>
<td>3.9$^{19}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zn$_2$S$_2$(ba)</td>
<td>3.9$^{19}$</td>
</tr>
<tr>
<td>CdS</td>
<td>2.3$^{19}$</td>
<td>Cd$_2$S$_2$(pa)</td>
<td>2.9$^{19}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cd$_2$S$_2$(ba)</td>
<td>2.9$^{19}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cd$_2$S$_2$(ha)</td>
<td>2.9$^{19}$</td>
</tr>
</tbody>
</table>

While it is obvious that the changes of inorganic frameworks directly affect the electronic structure, in the ionic systems the orbitals in the organic ligands are far removed from the band edges. Although the ligands can influence the polyhedral tilting of the lattice, if the inorganic polyhedral connectivity remains intact, altering the ligand, such as increasing the alkyl chain length, often leads to minimal changes to the band gap energies (Table 1.2)$^{19,78}$. 
Figure 1.5 Measured values for the cross-planar thermal conductivity of unmodified Na-montmorillonite clay and organoclay nanolaminates prepared from varying alkylammonium chain lengths.\textsuperscript{79} Reprinted with permission from ref. 79. Copyright 2013 American Chemical Society.
The thermal properties of atomic-scale materials, are dominated by the phonon transport within the framework, and will be quite different than the parent material\textsuperscript{80}. One of the major differences is the increase in number of organic-inorganic interfaces, which increases phonon scattering and can lead to materials with ultralow thermal conductivities even exceeding the "amorphous limit"\textsuperscript{81}. Losego \textit{et al.} reported that organoclay nanolaminates (alkylammonium cations intercalated aluminasilicate layers) have ultralow cross plane thermal conductivities of 0.08 W m\textsuperscript{-1} K, five times lower than the original clay, due to the increasing interface density\textsuperscript{79}. Also, the thermal conductivity is relatively independent with the lengths of the alkylammonium cations. However, in other dimensionally-reduced systems, like ZnTe(diamine) 2D frameworks, Huang \textit{et al.} discovered that the thermal conductivity of pressed pellets is significantly lower than 3D ZnTe, and decreases with increasing alkyl chain length\textsuperscript{82}.

Another interesting change takes place in the thermal expansion coefficients of these dimensionally-reduced hybrid materials. While most inorganic materials exhibit positive thermal expansion, some show negative, or zero thermal expansion\textsuperscript{83-84}. Li \textit{et al.} demonstrated that organic components (amine ligands) make a huge contribution in tuning the thermal expansion properties of a hybrid material. In the 2D ZnTe(diamine) frameworks, the \textit{a} and \textit{b} directions of the lattice still exhibit a positive expansion, but the \textit{c} direction shows a very small negative (nearly zero) thermal expansion, resulting from the combination of the positive inorganic expansion and the negative response of the diamine ligands\textsuperscript{85}. 
The magnetic properties of a material strongly depend on the coupling of localized electron spins within the lattice. Dimensionally-reduced derivatives provide a unique opportunity to study such magnetic interactions within single isolated layers or chains\cite{86}. The organic components of the structure not only preserve the bonding within the inorganic fragments, they also separate the inorganic layers or chains at tunable distances, making it possible to control the magnetic coupling through changing the structure via different ligands.

![Figure 1.6](image.png)

**Figure 1.6** Temperature dependent magnetic susceptibility data of different Fe$_3$Se$_4$(amine) structures.\cite{63} Reprinted with permission from ref. 63. Copyright 2015 Royal Society of Chemistry.
An example of the influence of the ligand on magnetic properties is shown in Figure 10 comparing three different Fe$_3$Se$_4$(amine) hybrid lattices$^{63}$. The dien ligand creates a structure where the inter-chain distances are greatest, leading to no interaction between the FeSe$_2$ chains and paramagnetic behavior with weak antiferromagnetic nearest-neighbor interactions. The structure with en ligands shows enhanced antiferromagnetic interactions within the chains and the interchain interactions also increased due to decreased interchain distances. In the Fe(tren) structure, there is a strong interaction between the Fe(tren) complex and the chains, which bends the angle between neighboring FeSe$_2$ tetrahedra along a chain producing weak ferromagnetic interactions. At the same time, the inter-chain distances are the shortest, and the 3D magnetic ordering between the chains becomes antiferromagnetic.

1.4 Applications of atomic scale derivatives

The creation of atomic-scale derivatives of solid-state lattices that feature completely different properties compared to the original material should have a cross-cutting impact in a diverse set of applications. However, most studies to date have focused on their performance in electronic and optoelectronic devices. Reducing the dimensionality of a solid-state lattice will typically increase the band gap energy, alter the absorption coefficients, and can change the nature of the gap from indirect to direct. In some cases, such as graphene and GeH, the carrier mobilities are significantly enhanced compared to the parent materials. These initial studies have exploited the changes in electronic structure,
the solution-processibility, and the mechanical flexibility of these materials for phosphors, FETs, and photovoltaics.

Figure 1.7 Room-temperature absorption (a) and emission (b) spectra of \([\text{Zn}_{1.7}\text{Cd}_{0.3}\text{S}_2}(L)]\) (L=pa, ba, ha, oa). (c) white-light LED aggregates made by coating a thin layer of sample on the surface of a 5 mm reference 360 nm LED: 1) illuminating reference UV LED, 2) the LED in (1) coated with a thin layer of [Zn$_{1.7}$Cd$_{0.3}$S$_2$(ha)] before illumination, 3) the LED in (2) illuminating, and 4) [Zn$_{1.7}$Cd$_{0.3}$S$_2$(ha)]:0.08%Mn]-coated LED illuminating.\textsuperscript{87} Reproduced with permission from ref 87. Copyright 2012 John Wiley and Sons.
Many of these dimensionally-reduced frameworks have increased band gaps, and enhanced photoluminescence, making them attractive phosphors for white light LEDs. For instance, the 2D ZnS(amine) based hybrid organic-inorganic semiconductors, doped with Cd and Mn have band gaps of 2.9 eV, with broad visible photoluminescence, and quantum yields of up to 37% (Figure 11 a,b). The quantum yield of these materials is already comparable to some commercially used phosphors.\textsuperscript{87} Dohner \textit{et al.} also showed that the 2D layered hybrid perovskite materials with the formula of (EDBE)PbX\textsubscript{4} (EDBE = 2,2’-(ethylenedioxy)bis(ethylammonium), X = Cl, Br, or I) can also emit white light, with a high color-rendering index and a photoluminescent quantum efficiency of 9\%.\textsuperscript{88} The broad white emission in both of these materials most likely originates mostly from defect trap states, with potentially some band edge emission as well. The different chromaticity coordinates and photoluminescence intensity can be further tuned via modification of either the inorganic or the organic components.

In the 1990’s and early 2000’s the 2D hybrid organic-inorganic perovskite materials were shown to be promising active electronic materials in thin film flexible FETs\textsuperscript{89}, due to their performance, ease of processing, low cost, and mechanical flexibility. Kagan \textit{et al.} fabricated thin film FET devices using a 300 Å thick solution processed (C\textsubscript{6}H\textsubscript{5}C\textsubscript{2}H\textsubscript{4}NH\textsubscript{3})\textsubscript{2}SnI\textsubscript{4} layer as the semiconducting channel. These devices showed field-effect mobilities of 0.62 cm\textsuperscript{2}/V s, and on-off ratios > 10\textsuperscript{4}, comparable to amorphous Si\textsuperscript{90}. Mitzi \textit{et al.} further improved the FET mobility up to 2.6 cm\textsuperscript{2}/V s, and on-off ratios of up to 10\textsuperscript{6}, using (3-MeOPEA)\textsubscript{2}SnI\textsubscript{4} and (4-MeOPEA)\textsubscript{2}SnI\textsubscript{4} (MeOPEA = methoxyphenethylamine) thin films and melt-processed FET channel layers\textsuperscript{91}.
In the past few years the methylammonium lead halide perovskites have revolutionized the field of solid-state thin film solar cells. The small band gaps, excellent absorption of visible light, the large carrier diffusion lengths, and the solution processability make these materials among the best performing candidates for solar energy conversion so far, with record efficiencies from 15-19\%\textsuperscript{92-96}, which is much closer to the Shockley-Queisser limit of \textasciitilde33\% for a single p-n junction solar cell. The dimensionally-reduced 2D perovskites have just started being explored as the active material in photovoltaics. Smith \textit{et al.} fabricated solar cells with an open-circuit voltage of 1.18 V and a power conversion efficiency of 4.73\% and enhanced moisture resistance compared to MAPbI\textsubscript{3} using (PEA)\textsubscript{2}(MA)\textsubscript{2}[Pb\textsubscript{3}I\textsubscript{10}] \hspace{0.1cm} (PEA=C\textsubscript{6}H\textsubscript{5}(CH\textsubscript{2})\textsubscript{2}NH\textsubscript{3}+, MA=CH\textsubscript{3}NH\textsubscript{3}+)\textsuperscript{97}. Whether these dimensionally-reduced materials can have improved photovoltaic performance\textsuperscript{98-99} or photoconductivity enhancements\textsuperscript{100} remains to be seen.

1.5 Chapter Outlines

The introduction in Chapter 1 is followed by Chapter 2, which presents the synthesis and characterization of the atomic scale derivatives of the titanium chalcogenide system. The crystal structures of four close related analogues (TiS\textsubscript{2}(en), TiS\textsubscript{2}(pn), TiSe\textsubscript{2}(en) and TiSeO(en)) were analyzed. The synthetic conditions of the derivatives were discussed and summarized in order to construct a synthetic phase diagram. Finally, the electronic band structures of these derivatives were compared with the original 2D lattice and within the four close related analogues.
In Chapter 3, the Li intercalation process in these dimensionally reduced van der Waals system were studied. The structural changes of the intercalation and deintercalation process were monitored using synchrotron X-ray and neutron diffractions. The chemical changes of the lattice were investigated and quantified by X-ray photoelectron spectroscopy (XPS) and a reversible change could be observed. A thin film device was fabricated and the electrical conductivity of the material before and after Li intercalation was studied at various temperature, indicating a large increase in electrical conductivity after intercalation and the semiconducting nature was at the same time preserved.

Chapter 4 focuses on the vanadium chalcogenide system. Results from a wide range of synthetic temperature window was investigated. Multiple new cluster and precursor phases were identified for both sulfides and selenides, including a $V_7S_8$ corner-sharing dicubane cluster. The electronic structure of the dicubane cluster was studied extensively using superconducting quantum interference device (SQUID) and electron spin resonance (EPR) spectroscopy, as well as density-function-theory (DFT) calculations, showing that the cluster contain only one unpaired electron. The results from this chapter underlines the rich chemistry of the vanadium chalcogenide system and provides a pathway for solution phase synthesis of 2D VS$_2$ and VSe$_2$ and other low temperature cluster and precursor phases.

The conclusions and the outlook of this thesis are summarized in Chapter 5.

References


80. Cahill, D. G.; Braun, P. V.; Chen, G.; Clarke, D. R.; Fan, S.; Goodson, K. E.; Keblinski, P.; King, W. P.; Mahan, G. D.; Majumdar, A.; Maris, H. J.; Phillpot, S. R.; Pop,


Chapter 2  One dimensional chain derivatives of titanium chalcogenides

2.1 Introduction

Layered metal dichalcogenides (LMDC) are one of the most well studied classes of materials due to their fascinating properties and applications\(^1\text{-}^9\). TiS\(_2\) is used as one of the first cathode materials in lithium ion battery and TiSe\(_2\), for example, is a semimetal\(^10\) that exhibits correlated electronic phenomena such as charge density waves\(^11\) as well as superconductivity upon Cu intercalation\(^12\). These materials share the same structure type as CdI\(_2\), and similar to the examples shown in the introduction chapter, they can be synthesized from the bottom-up to create the atomic scale derivatives of the original 2D lattice.

Similar to how carbon can be sculpted into low-dimensional allotropes such as fullerenes\(^13\), nanotubes\(^14\), graphene\(^15\), and graphene nanoribbons\(^16\), there is an emerging body of work suggesting that the framework connectivity of atoms for any crystalline solid can be ligand-terminated along specific axes to create stable, crystalline van der Waals solids comprised of single or few atom thick fragments\(^17\text{-}^20\). Indeed, dimensionally reduced solids have been discovered from the perovskite lattice\(^21\text{-}^22\), zinc blende/wurtzite lattice\(^23\), 2D metal chalcogenide lattice\(^24\text{-}^25\), and layered iron selenide lattice\(^26\). These dimensionally

reduced phases are thermodynamically stable because, for a set of metal cation and anion with specific oxidation states, there is some inherent stability for a specific type of polyhedral shape and connectivity\textsuperscript{20}. For example, in ZnS and numerous dimensionally reduced ZnS derivatives, Zn exhibits tetrahedral coordination and corner sharing connectivity partly because the Zn\textsuperscript{2+} and S\textsuperscript{2-} oxidation states, radius ratio, and electronegativity difference remain unchanged\textsuperscript{23}. These dimensionally reduced systems have different optical, electronic and magnetic behavior compared to the parent lattice\textsuperscript{24},\textsuperscript{26}, making them potentially interesting in phosphors and battery electrodes\textsuperscript{27-28}. These properties can be further tuned by changing the dimensionality, choice of ligand, and metal intercalation into the van der Waals gap.

In contrast to the solution-phase growth of colloidal semiconducting nanocrystals which has experienced over thirty years of scientific exploration\textsuperscript{29-34}, the synthesis of dimensionally reduced solids is still in its infancy. While one can envision the existence of different ligand terminated dimensionally reduced structures from a given lattice framework\textsuperscript{20}, there are very few formalized strategies to synthesize these phases. The most common approaches deliver molecular precursors of the metal and anion in the appropriate oxidation states, in the presence of organic terminating ligands\textsuperscript{24,35}. Here a large parameter space exists including ligand choice, ligand to metal ratio and reaction temperature. It is unclear how these parameters can be tuned to access the dimensionally reduced phases rather than the parent material.

Here, we develop a systematic understanding of the relative effect of ligand to metal ratio, reaction temperature and ligand choice on the synthesis of dimensionally reduced
TiS$_2$(en) \((en=\text{ethylenediamine})\) as a model system. We demonstrate that TiS$_2$(en) is preferred over the 2D LMDC (layered metal dichalcogenide) framework at a high ligand to metal ratio across a wide range of temperatures. The organic ligand plays a profound role in determining the thermodynamic stability of the structure. Changing the ligand from \textit{en} to \textit{propylenediamine} \((pn)\) significantly narrows the temperature window where the dimensionally reduced product is favored. This change from \textit{en} to \textit{pn}, however, only slightly perturbs the electronic structure and increases the band gap from 1.71 to 1.75 eV. The Se and the oxyselenide analogues can also be prepared using the same method. They also exhibit the 1D zigzag chain structure and the rhombohedral unit cell. However, the band gap of the Se analogue is much smaller (1.2 eV) and it also shifts from an indirect gap in TiSe$_2$ to a direct gap in the atomic scale derivatives.

\section*{2.2 Experimental section}

\subsection*{2.2.1 Preparation of TiS$_2$(en), TiS$_2$(pn), TiSe$_2$(en) and TiSeO(en)}

All synthetic procedures were conducted in dried N$_2$ either using standard Schlenk line techniques, or in a glove box. In a typical reaction of TiS$_2$(en), 0.3 g sulfur powder was dissolved in 10 mL \textit{en} that quickly turned into a dark red solution.\textsuperscript{36} 0.5 mL TiCl$_4$ was diluted in 2 mL dried chlorobenzene then immediately injected into the sulfur solution. The solution was later transferred to a Teflon cup in a Parr reactor in a dry N$_2$ atmosphere. The reactor was sealed and placed in a vacuum oven under evacuation and annealed at 220 °C for 5 days (Equation 1). TiS$_2$(pn) was synthesized following the same procedure except propylenediamine was used instead of ethylenediamine. In both the TiS$_2$(en) and TiS$_2$(pn)
systems, organic ligand to Ti ratio and annealing temperature were varied in order to obtain different phases and construct the synthetic phase space diagrams.

**Equation 1** Reaction of TiCl$_4$ and S powder in $en$ to form TiS$_2$(en).

\[
\text{TiCl}_4 + 2\text{S} + \text{excess } en \rightarrow \text{TiS}_2(en) + 2en \cdot 2\text{HCl}
\]

In a typical reaction of TiSe$_2$(en), selenium powder (0.719 g, 2.0 mmol) and NaBH$_4$ (0.345 g, 2.0 mmol) was dissolved in en (8.0 mL, 118 mmol) that quickly turned into a dark brown solution. TiCl$_4$ (0.5 mL, 0.5 mmol) was injected into the solution with dried chlorobenzene (1 mL, 10 mol) at room temperature. After heating at 180 ºC for 2 hours, the solution was transferred to a Teflon cup in a Parr reactor in a dry N$_2$ atmosphere. The reactor was sealed and placed in a vacuum oven under evacuation and annealed at 220 ºC for 5 days (**Equation 2**). For TiSeO(en), 8.6 µl H$_2$O was added before annealing at 220 ºC.

**Equation 2** Reaction of TiCl$_4$ and Se powder reduced by NaBH$_4$ in $en$ to form TiSe$_2$(en).

\[
\text{TiCl}_4 + 2\text{Se} + 4\text{NaBH}_4 + \text{excess } en \rightarrow \text{TiSe}_2(en) + 4\text{NaCl} + 2\text{H}_2 + 2en \cdot 2\text{BH}_3
\]

The crude gel-like products were transferred from the Parr reactor into a centrifuge tube in a glovebag filled with dry N$_2$. Approximately 30 mL of dried $i$-PrOH was added to recrystallize the product and wash out the salt byproduct (en·2HCl or pn·2HCl). The upper supernatant was removed after centrifugation at 2000 rpm for 10 min using a Thermofisher CL2 centrifuge. This procedure was repeated at least five times. The purified final product
was evacuated in a Schlenk line for at least 3 h to remove residual solvent and then stored in a glovebox.

2.2.2 Physical Characterizations

X-ray diffraction patterns were collected on powder samples of TiS$_2$(en), TiS$_2$(pn), TiSe$_2$(en) and TiSeO(en) using a Rigaku Miniflex powder diffractometer (30 kV, 15 mA, Cu X-ray tube, 293K). Diffraction data used in the Rietveld refinement was collected using a Bruker D8 powder diffractometer (40 kV, 50 mA, sealed Cu X-ray tube). The powder sample was sealed in 0.8 mm outer diameter glass capillary tube for measurement. Rietveld analysis was performed using the GSAS and TOPAS software package. The structure was solved without refining the H atom positions.

Elemental Analysis of the C/H/N ratio of both product was performed by Galbraith Inc., The actual and (theoretical) % mass for each element is TiSe$_2$(en): C 9.03 (8.89), H 3.01 (2.36), N 10.05 (9.64); TiSeO(en): C 11.8(10.3), H 3.94(3.47), N 13.8(11.2).

X-ray fluorescence measurements were performed using a DELTA Handheld X-ray fluorescence Analyzer. Standard samples were prepared by mixing TiO$_2$ and Se powder at the ratio of 1:0.5, 1:1, 1:1.5, 1:2, 1:2.5.

Thermogravimetric Analysis of TiSe$_2$(en) in flowing N$_2$ showed the product was stable up to 250 °C, above which en loss occurs.

Raman spectra was collected using a Renishaw InVia Raman equipped with a CCD detector. The Raman spectra were collected using 785 nm (near IR diode laser) illumination and scanning from 100-4000 cm$^{-1}$. 
Room-temperature photoluminescence (PL) experiments were conducted on a home-built instrument utilizing an InGaAs detector. The sample was excited at 785 nm using a diode laser, and a RG800 long pass filter was placed between the sample and the detector. Measurements at room temperature were carried out using a sample suspension in quartz cuvettes. Measurements at 77 K were carried out in quartz NMR tubes, frozen using liquid nitrogen.

Diffuse reflectance absorption spectra were collected using a Lambda 950 spectrophotometer (Perkin-Elmer) with a 60 mm integrating sphere. Spectra were collected with 1 nm resolution.

2.2.3 Density-function-theory calculations

For TiS$_2$(en) and TiS$_2$(pn), electronic band structure calculations were performed using density functional theory as implemented in the WIEN2k package$^{37}$. H positions in each rhombohedral lattice were estimated using structural information from Rietveld refinement of the powder x-ray diffraction data. The structures were then optimized with WIEN2k's “MSR1a” mixing scheme, which simultaneously converges charge densities and atomic positions. Electronic band diagrams were generated by self-consistent calculation of the Kohn-Sham orbital energies on a 6x6x6 Monkhorst pack in the irreducible wedge of the Brillouin zone. The modified Becke-Johnson exchange-correlation potential was selected on the basis of its previously reported accuracy for
determining semiconductor band gaps\textsuperscript{38-40}. Each calculation was iterated until the total energy converged within 0.0001 Ry and the charge converged within 0.00005 eV.

For TiSe\textsubscript{2}(en), DFT related calculations were executed using the Cambridge Serial Total Energy Package, a sub-program of Materials Studio (Accerlys, Inc; San Diego, California, USA). Calculations were performed using the reduced rhombohedral unit cell and along the RHL2 k-space pathway of the Brillouin zone. A norm-conserving non-local pseudopotential generated by the Kerker scheme with an energy cutoff of 400 eV was utilized. An energy charge per atom convergence criterion of 0.00002eV, a root-mean-square displacement of 0.001 Å, and a root-mean-square residual force on movable atoms of 0.05eV/Å was chosen. Electron exchange interactions and correlation were developed by Wu and Cohen via a generalized gradient approximation. The positions of the H atoms were initially estimated based off of the known bond lengths and bond angles of ethylenediamine. The structure was geometry optimized using the Broyden-Fletcher-Goldfarb-Shanno scheme, which enabled optimization of both the lattice parameters and the atomic coordinates. Starting positions for the geometry optimization were given from the results of Rietveld refinement.

2.3 Crystal structures of the 1D chain derivatives of titanium chalcogenides

2.3.1 The structures of TiS\textsubscript{2}(en) and TiS\textsubscript{2}(pn)

There exist at least two different phases of TiS\textsubscript{2}-amine derivatives, including ones with 2D\textsuperscript{41-42} and 1D\textsuperscript{24} octahedral connectivity (Figure 2.1 a, c and e). It has been well
documented that organic amines can be intercalated into the 2D TiS₂ lattice (Figure 2.1 e). The short chain (C1-C4) amine molecules lie parallel with the TiS₂ layer⁴³.

Figure 2.1 Crystal structures of (a) TiS₂(en) and (b) TiS₂(pn) projected down the c axis. Ti octahedra are shaded in blue. (c) TiS₂(en) and (d) TiS₂(pn) chains along the c axis. (e) en intercalated TiS₂ layers. Atom colors: Ti, blue; S, yellow; N, green; C, black. H atoms are omitted for clarity.
In addition, we have recently created TiS$_2$(en), a single octahedral thick 1D derivative (Figure 2.1 a, c). This structure consists of 1D edge-sharing Ti octahedra that run parallel to the c axis. Each Ti atom is coordinated by 4 S atoms and two N atoms distorted away from a perfect octahedron. Neighboring octahedra are connected by two bridging S atoms. The Ti atom is also coordinated to a cis-binding bidentate ligand, en. These chains are held together via van der Waals forces and packed into a hexagonal arrangement. This phase adopts an R-3c unit cell with 3-fold helicity and the unit cell parameters are shown in Table 1. Here we demonstrate that a similar dimensionally reduced 1D phase can be created with pn (Figure 2.1 b, d). This TiS$_2$(pn) phase also crystallizes into an R-3c unit cell with an expanded a axis and slightly contracted c axis (Table 2.1). The structure of this analogue is solved using GSAS software package and the diffraction pattern data and the Rietveld results can be seen in Figure 2.2 and Table 2.2. The average Ti-S bond length is 2.360 Å which is slightly larger than that 2.336 Å in TiS$_2$(en) (Table 2.3).

<table>
<thead>
<tr>
<th>Table 2.1 Unit cell parameters of TiS$_2$(en) and TiS$_2$(pn)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit cell parameter</td>
</tr>
<tr>
<td>TiS$_2$(en)</td>
</tr>
<tr>
<td>TiS$_2$(pn)</td>
</tr>
</tbody>
</table>
Figure 2.2 Powder x-ray diffraction pattern Rietveld refinement of TiS$_2$(pn). Observed data, calculated patterns, and the difference curves are plotted as red, green, and pink, respectively. The 2-Theta reflections are shown in black.

Table 2.2 GSAS Rietveld Refinement results for TiS$_2$(pn)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>TiS$_2$C$<em>3$H$</em>{10}$N$_2$</td>
</tr>
<tr>
<td>$F_w$</td>
<td>176.07</td>
</tr>
<tr>
<td>Space Group</td>
<td>R-3c</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>20.3062(11)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>8.9094(5)</td>
</tr>
<tr>
<td>Cell Volume (Å$^3$)</td>
<td>3181.55(31)</td>
</tr>
<tr>
<td>$T$ (K)</td>
<td>295</td>
</tr>
<tr>
<td>$\lambda$ (Å)</td>
<td>1.5406</td>
</tr>
<tr>
<td>pattern range (2θ, °)</td>
<td>7-60</td>
</tr>
<tr>
<td>step size (2θ, °)</td>
<td>0.0008</td>
</tr>
<tr>
<td>step scan time (s)</td>
<td>5</td>
</tr>
<tr>
<td>$R_{exp}$</td>
<td>0.0719</td>
</tr>
<tr>
<td>$R_{wp}$</td>
<td>0.0427</td>
</tr>
<tr>
<td>$R_p$</td>
<td>0.0340</td>
</tr>
</tbody>
</table>
Table 2.3 Representative bond lengths in TiS$_2$($en$) and TiS$_2$($pn$)

<table>
<thead>
<tr>
<th></th>
<th>Ti-S1 / Å</th>
<th>Ti-S2 / Å</th>
<th>Average Ti-S / Å</th>
<th>Ti-N / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiS$_2$($en$)</td>
<td>2.308</td>
<td>2.364</td>
<td>2.336</td>
<td>2.277</td>
</tr>
<tr>
<td>TiS$_2$($pn$)</td>
<td>2.359</td>
<td>2.360</td>
<td>2.360</td>
<td>2.280</td>
</tr>
</tbody>
</table>

2.3.2 The structures of TiSe$_2$($en$) and TiSeO($en$)

Both TiSe$_2$($en$) and TiSeO($en$) have a similar crystalline structure to TiS$_2$($en$) reported previously$^{24}$ (Figure 2.3 a, b). The Ti:Se stoichiometry for both samples was confirmed via X-ray fluorescence (Figure 2.4) and the 2:8:2 C:H:N ratio was confirmed by elemental analysis.

The crystal structures were determined via Rietveld refinement of X-ray powder diffraction patterns using TOPAS Academic software package (Figure 2.5-2.7). Both phases adopt a Rhombohedral unit cell (R-3c space group) with unit cell parameters shown in Table 1. Compared to TiS$_2$($en$), the $a$ parameter for TiSe$_2$($en$) and TiSeO($en$) increase by 0.2 Å and 0.3 Å, respectively whereas the $c$ axis increases by 0.3 Å and decreases by 0.2 Å, respectively. For TiSe$_2$($en$) these changes are consistent with replacing S with the larger Se.
Figure 2.3 View of (a) TiSe\(_2\)(en) and (b) TiSeO(en) down the c axis. Distorted octahedron of (c) TiSe\(_2\)(en) and (d) TiSeO(en). (e) TiSeO(en) chain along c axis.

Figure 2.4 X-ray fluorescence results of Se/Ti ratio in TiSe\(_2\)(en) and TiSeO(en). Red line: linear fitting of standard sample mixtures.
Table 2.4 Lattice parameters and band gap energy for TiS$_2$(en), TiSeO(en) and TiSe$_2$(en)

<table>
<thead>
<tr>
<th></th>
<th>a/Å</th>
<th>c/Å</th>
<th>E$_g$ /eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiS$_2$(en)</td>
<td>18.596(1)</td>
<td>9.0158(1)</td>
<td>1.70</td>
</tr>
<tr>
<td>TiSeO(en)</td>
<td>18.800(2)</td>
<td>8.8154(9)</td>
<td>1.21</td>
</tr>
<tr>
<td>TiSe$_2$(en)</td>
<td>18.990(1)</td>
<td>9.3260(3)</td>
<td>1.21</td>
</tr>
</tbody>
</table>

The refined structures consist of zigzag 1D edge sharing chains of Ti octahedra that run parallel to the c axis, due to the incorporation of the cis-binding bidentate ligands into the framework. Neighboring octahedra are connected by two bridging Se atoms for TiSe$_2$(en) or one Se atom and one O atom for TiSeO(en). Within each octahedron, the Ti atom is coordinated by four Se atoms (two Se atoms and two O atoms for TiSeO(en)) and two N atoms from the ligand (Figure 2.3 c, d). Bond angles in the octahedra are distorted away from 90° due to the limitation of the length of the en molecule. The gauche conformation of the en ligand$^8$ was confirmed by Raman spectroscopy (Figure 2.8). Each 1D chain features a 3-fold periodicity along the c axis (Figure 2.3 e).
Figure 2.5 Powder X-ray diffraction patterns of TiSe$_2$(en) (black) and TiSeO(en) (red)
Figure 2.6 Rietveld refinement of TiSeO\((en)\). Observed data, calculated patterns, and the difference curves are plotted as black, red, and grey lines, respectively.

Figure 2.7 Rietveld refinement of TiSe\(_2\)(en). Observed data, calculated patterns, and the difference curves are plotted as blue, red, and grey lines, respectively.
In TiSeO(en), Se and O anions are ordered at distinct sites, based off of Rietveld analysis. Three structures were considered as starting models: 1. O only occupies the trans sites; 2. O only occupies the cis sites; and 3. O/Se atoms are disordered at both sites. The best refinement had the O atoms trans to each other and the Se atoms cis to each other. This gives the Ti-Se and Ti-O bond lengths 2.5058(79) Å and 2.148(17) Å. No significant improvement was observed by introducing O/Se disorder, which gave comparable $R_{wp}$ (weighed profile R-factor, used to evaluate the goodness of fit) values but unreasonable thermal parameters with only 8 percent disorder. Thus, we are confident that the Se and O atoms are ordered in the structure. The refined positions of oxygen further explain why TiSeO(en) has a smaller $c$ parameter than TiS$_2$(en). The Ti-Se-Ti and Ti-S-Ti bond angles in TiSe$_2$(en) and TiS$_2$(en) are close to 90°. By substituting one Se atom in every edge
sharing pair for an O atom, the mismatch in the lengths of the Ti-O and Ti-Se bonds causes the Ti-O-Ti angle to open up and the Ti-Se-Ti angle to compress (Figure 2.9). The presence of much shorter Ti-O bonds reduced the distance between Ti atoms in the c-direction thereby reducing the c parameter.

![Diagram showing Ti-S-Ti, Ti-Se-Ti, and Ti-O-Ti bond angles](image)

**Figure 2.9** Ti-S-Ti bond angle in TiSe$_2$(en) (left), Ti-Se-Ti bond angle in TiSe$_2$(en) (middle) and Ti-O-Ti, Ti-Se-Ti bond angles in TiSeO(en) (right).

### 2.4 Synthetic phase diagrams of the titanium sulfide systems

In the Ti-S system, considering both 2D and 1D TiS$_2$ frameworks exist, we wanted to develop a roadmap to synthetically access each phase using *en* as the coordinating ligand. In this approach we delivered soluble molecular precursors of Ti$^{4+}$ via TiCl$_4$ and S$^{2-}$ via a combination of S and organic diamine. It is well established that amines act as sacrificial
agents to reduce the S to S\(^2\)\(^{-36}\). We varied the temperature and ligand to metal ratio of the reaction and identified the product phases using powder X-ray diffraction (XRD). The resulting synthetic phase space diagram is illustrated in Figure 2.10 (a). Representative powder X-ray diffraction patterns of each product phase are found in Figure 2.10 (b).

![Synthetic phase space diagram of TiS\(_2\) (en) system. Red, intercalated TiS\(_2\); orange, mixed phases; green, TiS\(_2\) (en); blue, amorphous. (b) Representative powder X-ray diffraction patterns of each phase.](image)

For a wide range of temperatures, from 80 to 220 °C, and at a high en:Ti ratio, the 1D TiS\(_2\) (en) dimensionally reduced product phase is favored. The TiS\(_2\) (en) hybrid phase is essentially phase pure between 80-220°C for ligand to metal ratios ranging from 30:1 to less than 10:1. At 220°C, the boundary between the 1D and intercalated phases occurs near a ligand to metal ratio of 6.5:1. This mixed phase region is comprised of both the 1D
TiS$_2$(en) phase and 2D intercalated TiS$_2$ phase. At 220 °C and with a ligand to metal ratio below 5, the pure 2D intercalated TiS$_2$ phase is produced. At 120 °C, the 1D TiS$_2$(en) phase is stable at ligand to metal ratios of 30:1 to 3:1, and an amorphous phase emerges when the ratio is reduced further. The boundary between the 2D intercalated and amorphous phases occurs at 155°C and does not pass through the 1D TiS$_2$(en) phase.

**Figure 2.11** (a) Powder X-ray diffraction patterns of products obtained via varying (en): Ti ratio; (i. 30:1, ii. 20:1, iii. 10:1). (b) Powder X-ray diffraction patterns of products obtained via varying temperature; (i. 220°C, ii. 180°C, iii. 140°C, iv. 100°C). en: Ti ratio 20:1.

Pure 1D TiS$_2$(en) exists in a large temperature and ligand to metal ratio phase space, we then further explored how the crystallinity changed as a function of these parameters. **Figure 2.11** (a) depicts the XRD spectra when synthesized at 220°C while decreasing the
ligand to metal ratio from 30:1 to 10:1. At this temperature, the full width at half maximum (fwhm) of the (110) peak varies from 0.0040 to 0.0055 radians. **Figure 2.11** (b) depicts the XRD spectra when synthesized at a ligand to metal ratio of 20:1 while decreasing the temperature from 220 to 100°C. A highly crystalline product can be obtained despite a change in synthesis temperature of over 100°C. Fwhm values of 0.0036, 0.0040, 0.0034, and 0.0035 radians were calculated for the first peak (110) of XRD spectra at 220, 180, 140, and 100°C, respectively. Thus, from the Debye-Sherrer equation, the crystalline domain size of the TiS$_2$(en) product is relatively uniform across several temperatures.

**Figure 2.12** (a) Synthetic phase space diagram of TiS$_2$(pn) system. Red, intercalated TiS$_2$; orange, mixed phases; green, TiS$_2$(pn); blue, amorphous. (b) Representative powder X-ray diffraction patterns of each phase.

We were also able to create a similar 1D TiS$_2$ structure using pn as the organic ligand. The reaction temperature and pn:Ti ratio were again varied to construct a synthetic phase
space diagram (Figure 2.12 (a)). Again, we observed four distinctive regions representing different phases: intercalated 2D TiS$_2$, mixture of 2D intercalated TiS$_2$ and 1D TiS$_2$(pn), pure 1D TiS$_2$(pn) and the amorphous product (Figure 4b). At high reaction temperatures, the intercalated product was predominant and stable for a wide temperature range. As the temperature lowered to 140°C, a mixture of the 2D and 1D phases were obtained. The pure 1D TiS$_2$(pn) phase can be isolated only between 120-130°C. Below 120 °C no crystalline phase can be identified. Varying the pn:Ti ratio from 30:1 to 15:1 does not change the phase that is formed at a specific temperature. Despite the structural similarity of 1D TiS$_2$(pn) and TiS$_2$(en), the synthetic conditions to obtain TiS$_2$(pn) are limited to a very narrow temperature window. This suggests that even though the difference in the organic ligand is small, it plays a profound role in determining the stability of the dimensionally reduced product.

A true phase diagram implies that different phases can be reversibly accessed by changing the temperature and ligand to metal ratio. To probe whether these phases are at a kinetically trapped state or a thermodynamic equilibrium, we performed two control experiments. First, one equivalent of en was added to 1D TiS$_2$(en) and annealed at 200 °C for 4 days. 2D intercalated TiS$_2$ was not formed despite that fact that it exists in this region of the diagram (Figure 2.13). Similarly, annealing the 2D product with 20 equivalents of en at 200 °C for 4 days did not generate any 1D TiS$_2$(en) (Figure 2.14).
Figure 2.13 1D TiS\textsubscript{2}(en) XRD patterns before (black) and after (red) annealed with additional one equivalent of en at 200 °C for 1d.
Figure 2.14 2D intercalated TiS₂ XRD patterns before (black) and after (red) annealed with additional 20 equivalents of \( en \) at 200 °C for 1d. The starred peak is from the aluminum holder.

Together both of these synthetic phase space diagrams illustrate numerous principles about the relative thermodynamics of a dimensionally reduced material and the original
framework. At high temperatures, the original 2D TiS$_2$ framework is thermodynamically preferred partly due to the increased entropy associated with the loss of a ligand. This effect is most pronounced in the TiS$_2$(pn) system, but is also apparent in the TiS$_2$(en) system when the $en$:Ti ratio is small (<5:1). In this case, the coordinating environment created by $en$ cannot inhibit the formation of the parent lattice TiS$_2$, therefore the 2D intercalated phase is formed. Furthermore, in the low-temperature regime for $pn$, and the low $en$ equivalent-low temperature region the temperature is not high enough to overcome the kinetically-trapped amorphous product. Finally, these experiments show that the nature of the organic ligand plays a significant role in determining the relative stability of the dimensionally reduced product. The 1D TiS$_2$(en) product can be readily synthesized across a much larger temperature range compared to the 1D TiS$_2$(pn) product.

### 2.5 Electronic band structures of the 1D sulfide and selenide analogues

The optical properties of TiS$_2$(en) and TiS$_2$(pn) were investigated using diffuse reflectance absorption (DRA) measurements. Both of these jet-black 1D materials exhibit broad absorption in the visible light range with an onset at near-infrared (NIR) energies (Figure 2.15 (a)). The band gap energy of TiS$_2$(en) and TiS$_2$(pn) was determined to be 1.71 and 1.75 eV, respectively, by linearly fitting the absorption edge of the plot of the Kubelka-Munk function ($F(R) = (1 - R)^2/2R$, where R is the measured reflectance). These values correspond to a 1.4 eV increase in band gap energy compared to 2D bulk TiS$_2$ which has an indirect band gap of 0.3 eV$^{44}$. 

60
Figure 2.15 (a) Diffuse reflectance spectra of both TiS$_2$(en) and TiS$_2$(pn). (b) Calculated band structure of TiS$_2$(en). (c) Partial density of states of Ti 3d (black) and S 3p (red) for TiS$_2$(en). (d) Calculated band structure of TiS$_2$(pn). (e) Partial density of states of Ti 3d (black) and S 3p (red) for TiS$_2$(pn).
This slight increase in band gap energy from TiS$_2$(en) to TiS$_2$(pn) indicates that changing the diamine ligands does not strongly influence the electronic structure of the material. This is confirmed by simulation of the band structures of both materials using the TB-mBJ exchange-correlation potential as implemented in WIEN2k. The band structure calculations for each trigonal lattice were performed using the reduced rhombohedral unit cell along the RHL2 Brillouin zone pathway. TiS$_2$(en) and TiS$_2$(pn) are calculated to have direct band gaps of 1.81 and 1.94 eV at $\Gamma$, respectively (Figure 2.15 (b), (d)). These values are in excellent agreement (6-11 % larger) with the observed experimental results. This is much more accurate than previous simulations of TiS$_2$(en) employing CASTEP (GGA-WC) which underestimate the band gap by 35%.

The partial density of states plots of TiS$_2$(en) and TiS$_2$(pn) (Figure 2.15 (c), (e)) show that the valence band maximum (VBM) is composed primarily of S 3p orbitals and the conduction band minimum (CBM) is composed primarily of Ti 3d orbitals. The N 2p orbitals for both materials lie much lower in energy than the VBM (<-2.5 eV) and do not strongly contribute to the conduction and valence band edges (Figure 2.16). Therefore, changing the amine ligand from en to pn has a minimal effect on the band structure considering that the polyhedral connectivity of the edge-sharing zigzag inorganic backbone remains unchanged. This phenomenon is similar to other previous studies on dimensionally reduced systems using different ligands\textsuperscript{22-23}. 
Figure 2.16 Partial density of states of (a) TiS$_2$(en) and (b) TiS$_2$(pn) showing Ti, S and N contributions.

The optical properties of TiSe$_2$(en) and TiSeO(en) were also investigated using DRA and PL measurements. The band gap energy for both compounds was determined to be 1.21 eV by linearly fitting the absorption edge on the plot of Kubelka-Munk function vs. photon energy. This value is 0.5 eV lower than the band gap of TiS$_2$(en) (1.7 eV). Furthermore, there is a 1.4 eV increase in band gap energy with respect to bulk TiSe$_2$, 63
which has a -0.2 eV overlap between conduction band and valence band.\textsuperscript{10} This 1.4 eV increase is almost exactly the same magnitude as the difference between TiS\textsubscript{2} and TiS\textsubscript{2}(en).

\textbf{Figure 2.17} (a) DRA absorption spectra of TiSe\textsubscript{2}(en), TiSeO(en) and TiS\textsubscript{2}(en). (b) Absorption (black) and NIR photoluminescence (red) of TiSe\textsubscript{2}(en)

NIR PL was observed from TiSe\textsubscript{2}(en) at room temperature (\textbf{Figure 2.17} (b)) and at 77 K (\textbf{Figure 2.19}) excited at 785 nm. In both conditions, above band gap emission was observed at 1.38 eV and 1.40 eV while an emission close to the band edge (1.20 eV) was also observed at room temperature. No PL was observed for TiSeO(en). Above band gap PL has been observed to occur for numerous materials including single and few layer MoS\textsubscript{2} and Tl\textsubscript{4}InGa\textsubscript{3}S\textsubscript{8}\textsuperscript{2}, when there are either defect states or low-lying bands that are relatively higher or lower than the energy of conduction band minimum or valence band maximum respectively, with direct transitions and short radiative lifetime.
Figure 2.18 (a) Local electronic band structure for TiSe$_2$(en). (b) Partial density of states, where s (blue), p (orange), and d (red) orbital contributions are summed (black). (c) Band structure illustrations of TiSe$_2$, TiSe$_2$(en) and TiSeO(en)
The simulated band structure of TiSe$_2$(en) further confirms the presence of numerous bands close in energy to the band gap. The electronic structure of TiSe$_2$(en) was calculated using CASTEP (GGA-WC). The result shows that both conduction band minimum and valence band maximum occur at the $\Gamma$ point (Figure 2.18 (a)), which indicates a direct band gap and is consistent with the observed PL. The band gap appears to be 0.706 eV, 42% lower than the measured value. This ~40% decrease is expected using this level of theory. For instance, previously we calculated the band gap of TiS$_2$(en) to be 35% lower than the measured gap. Attempts to simulate the band structure of TiSeO(en) using different level of theory including GGA and LDA proved unsuccessful as the geometry
optimization always gave unrealistic Ti-O bond distance (~1.8 Å). Additionally the refined crystal structures were used to calculate the band structure for all three compounds however TiSeO(en) still gave a significantly higher simulated band gap than the other two. We suspect that the lack of PL in TiSeO(en) is due to a change from direct to indirect band gap and elimination of correlated low-lying bands.

**Figure 2.20** Calculated electronic partial densities of states (PDOS) of Ti, N and Se in TiSe₂(en) at room temperature

The partial density of states plots for specific atoms (**Figure 2.20**) reveal that the conduction band is mainly composed of unoccupied Ti 3d orbitals and we see a segregation of two sets of bands. The 18 lower energy bands (0.7-2.5 eV) shown in the band diagram in **Figure 2.18** (a) are comprised of three Ti 3d orbitals (t₂g), while higher energy bands
(2.5-4 eV) are comprised of two other 3d orbitals ($e_g$). The valence band maximum is predominately composed of Se 4p non-bonding orbitals while the N 2p bonding orbitals lie below at -3 eV.

TiSeO($en$) has the same band gap as TiSe$_2$($en$), suggesting that the position of the top of the valence band is not changed despite the fact half of the Se atoms are replaced with O atoms. Because oxygen is more electronegative than selenium, the O 2p non-bonding bands will appear at lower energy than the Se bands (Figure 2.18 (c)). However the density of Se 4p states near the band edge should be reduced, which explains why TiSeO($en$) has a reduced absorption near the band edge than TiSe$_2$($en$).

2.6 Conclusion

Using TiS$_2$ as a model system, we have demonstrated that dimensionally reduced phases can be created using solution phase processes at large ligand-to-metal ratios and lower temperatures. The parent structure is more stable at higher temperature likely due to the increasing entropy. The temperature window at which the dimensionally reduced phase is produced is ultimately determined by the organic ligand. Even extending the ligand alkyl chain length by a single carbon atom can profoundly narrow the temperature window at which these phases are accessed. However, extending the alkyl chain length does not change the metal-ligand bond characters and therefore will only marginally change the electronic structure of the material. In summary, this systematic understanding of the influence of ligand structure, reaction temperature, and ligand to metal ratio lays the foundation for the rational synthesis of dimensionally reduced phases.
We have also created for the first time dimensionally reduced hybrid zigzag structures of TiSe$_2$(en) and TiSeO(en) which consist of 1D edge-sharing Ti octahedra chains. Both materials have a 1.21 eV band gap whereas TiSe$_2$(en) has a direct gap with NIR photoluminescence. Interestingly, the 1.4 eV increase in band gap from TiSe$_2$ to TiSe$_2$(en) is of the same magnitude as TiS$_2$ to TiS$_2$(en), which implies that dimensional reduction can be applied to different metal chalcogenide lattices with a predictable and systematic change in band structure.

**References**


Chapter 3  
Reversible Li intercalation in the 1D chain derivative TiS$_2$(en)

3.1 Introduction  

The intercalation of polymers, small molecules, and metals inside the van der Waals gap of 2D solids is one of the most powerful approaches for tuning the electronic, magnetic, and correlated properties to realize interesting physical phenomena and applications$^{1-22}$. For example, it has been well established that metals can be intercalated inside layered transition metal dichalcogenides (LMDCs) to create superconductors$^{22-24}$, thermoelectric materials$^{25-26}$, charge density waves$^{27-28}$, and Li ion battery electrodes$^{29-35}$. Li intercalation in these LMDCs reduces the chalcogenide host, with the electrons filling the the metal d-orbital based conduction band, with the resulting Li$^+$ resides on the octahedral hole sites in the van der Waals gap$^{2,36-37}$. The feasibility of Li intercalation in the narrow band gap semiconductor, TiS$_2$, made it one of the first Li battery cathode material candidates$^{38-39}$. 

There is an emerging body of work suggesting that the polyhedral connectivity of atoms for any crystalline framework can be ligand-terminated along specific axes to produce stable, crystalline dimensionally reduced van der Waals solids that have single to few atom thicknesses$^{40-45}$. These dimensionally-reduced derivatives have fundamentally different properties, compared to the original lattice, such as conversion from indirect to direct band gaps$^{42}$, efficient white light emission$^{46}$, and unique magnetic behavior$^{47}$. Being able to

---

intercalate metal cations and donate electrons inside a dimensionally reduced hybrid lattice could similarly enable the rational manipulation of their electronic and magnetic properties. Still, the intercalation and deintercalation of metal cations inside a dimensionally-reduced hybrid organic/inorganic lattice has yet to be demonstrated. Herein, we show that 1 equivalent of Li can be intercalated inside TiS$_2$(en), a dimensionally-reduced 1D transition metal dichalcogenide derivative, which reduces the Ti$^{4+}$ framework to Ti$^{3+}$, and leads to a significantly enhanced electrical conductivity.

We have recently created TiS$_2$(en), the dimensionally reduced one-dimensional (1D) derivative of a layered metal dichalcogenide lattice$^{42}$. TiS$_2$ normally crystallizes into the CdCl$_2$ structure type, consisting of layers of edge sharing TiS$_6$ octahedra. The TiS$_2$(en) lattice is derived by removing four of the six neighboring octahedra in a single layer, resulting in 1D zigzag edge sharing chains. The two nonedge-sharing S atoms on each Ti-S octahedron are substituted with a bidentate en ligand. The chains are twisted into a three-fold helicity, and held together via van der Waals forces (Figure 1a). The crystal structures were determined using Rietveld refinements of 2 K neutron diffraction data which will be described further. The 0.3 eV indirect band gap$^{48}$ of TiS$_2$ is converted into a 1.7 eV direct band gap in TiS$_2$(en).

3.2 Experimental section

3.2.1 Synthesis and purification of TiS$_2$(en)

All synthetic procedures were conducted in dried N$_2$ either using standard Schlenk line techniques, or in a glove box. In a typical reaction, sulfur powder (1.3 g, 4.1 mmol) was
dissolved in en (5.0 mL, 74 mmol) that quickly turned into a dark red solution. TiCl₄ (2 mL, 2 mmol) was diluted in dried chlorobenzene (8 mL, 80 mol) then immediately injected into the sulfur solution. The solution was later transferred to a Teflon cup in a Parr reactor in a dry N₂ atmosphere. The reactor was sealed and placed in a vacuum oven under evacuation and annealed at 200-220° C for 5 days.

The crude gel-like TiS₂(en) product was transferred from the Parr reactor transferred into a centrifuge tube in a glovebag filled with dry N₂. Approximately 30 mL of dried i-PrOH was added to recrystallize the product and wash out the salt byproduct (en·2HCl). The upper supernatant was removed after centrifugation at 2000 rpm for 10 min using a Thermofisher CL2 centrifuge. This procedure was repeated at least five times. The purified final product was evacuated in a Schlenk line for at least 3 h to remove residual solvent and then stored in a glovebox.

3.2.2 Li intercalation and deintercalation

The intercalation of LiTiS₂(en) was conducted in a glovebox. 0.5 g of dried TiS₂(en) was dispersed in 50 mL dry hexane and stoichiometric amounts (0.33, 0.67 and 1.02 equivalent moles) of n-butyl Lithium hexane solution were prepared in 50 mL dry hexane. The n-butyl lithium solution was added to the 50 mL TiS₂(en) suspension and heated up at 50 ° C for 24 hours. The powder was then centrifuged and washed with 30-50 mL of dry hexane in the glovebox 5 times. The final product was evacuated in a Schlenk line for at least 3 hours remove residual solvent.
Deintercalation was performed by washing LiTiS$_2$(en) in 0.1 M I$_2$ THF solution with the equivalent amount of I$_2$ with respect to Li. The powder was then further washed using dried THF 3 times followed by vacuum drying.

3.2.3 Elemental analysis

Elemental ratios of Ti and Li were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Perkin-Elmer Optima 3000DV analyzer. A trace amount (6.3 mg) of LiTiS$_2$(en) was digested with an aqua regia solution in a sealed vial at room temperature for at least 6hr and then diluted by a factor of 10$^4$ using Deionized water, resulting in linear concentration ranges between 0.5 and 30 ppm for an individual element. The actual elemental ratios of Ti:Li is found to be 1.00:1.05 (in comparisons with theoretical ratios of 1:1). C, H, N, and S elemental analysis of LiTiS$_2$(en) was performed by Atlantic Microlab, Inc (Norcross, GA) using LECO 932 CHNS analyzers, respectively. The solid samples of 15-20 mg were securely sealed in a capped vial under N$_2$ atmosphere prior to the shipment and the combustion analyses. The actual and (theoretical) % mass for each element is C: 13.9 (13.4), H: 4.9 (4.5), N: 14.1 (15.7) and S: 30.0(35.8).

3.2.4 Powder X-ray diffraction

X-ray diffraction patterns were collected on powder samples of TiS$_2$(en) and Li$_x$TiS$_2$(en) using a Bruker D8 powder diffractometer (40 kV, 50 mA, sealed Cu X-ray tube, 293K) and the 11-BM-B beamline at the Advanced Photon Source at Argonne National Laboratory (wavelength: 0.413248 Å, 100 K). The powder samples were sealed
in 0.8 mm outer diameter glass capillary tubes inside a glovebox prior to the measurements. Rietveld analysis was performed using the TOPAS and GSAS software package. The structure was solved without refining the H atom positions.

3.2.5 Powder neutron diffraction

Neutron-scattering data were collected at 2 and 300 K using the time-of-flight (TOF) instrument POWGEN beamline 11-A at the Spallation Neutron Source, Oak Ridge National Laboratory. The powder samples (1.0-1.5g) were loaded into a vanadium can having 1/4 inch outer-diameter and filled to 2-inches in lengths inside a glovebox prior to the measurements. Rietveld analysis of the data was performed using the GSAS software package. The structure was solved refining the positions of all atoms including the H and Li atoms. The thermal broadening U_{iso} parameters were fixed for all elements, due to small range of high d values collected.

3.2.6 X-ray photoelectron spectroscopy (XPS) measurement

XPS was collected using a Kratos Axis Ultra X-ray photoelectron spectrometer equipped with a monochromated (Al) X-ray gun at 12.0 kV and 10 mA. Survey spectra were scanned at 100 ms dwell for 2 sweeps. Ti and Li spectra were scanned at 250 ms dwell for 8 sweeps. The C and O peaks in the survey spectra are ubiquitous contaminants in the XPS instrument.
3.2.7 Thin film device fabrication and characterization

Glass substrates were cleaned by sonication in acetone and isopropanol for 30 min and then blown dried and O\textsubscript{2} plasma cleaned for 5 min. 0.1 g of TiS\textsubscript{2}(en) were dispersed in 0.5 ml MeOH and 0.5 ml isopropanol mixture by bath sonication for 1 hour. The suspension was then allowed to settle for another hour and the upper half of the suspension was used for a 2\textsuperscript{nd} round of sonication. This process was repeated three times. Thin films of TiS\textsubscript{2}(en) on glass substrates were prepared by doctor-blading two drops of suspension across a scotch tape mask. LiTiS\textsubscript{2}(en) thin films were prepared by soaking the as-prepared TiS\textsubscript{2}(en) films in excess n-BuLi hexane solution for 1 day then rinsed in hexane five times.

The average thickness of the TiS\textsubscript{2}(en) films were measured using an Alpha-Step D-100 Profilometer (KLA-Tencor, Milpitas, CA) and observed to be 4.8 µm. Electrical transport measurements were performed on a Lakeshore CPX Cryogenic Probe Station using ZN50R-CVT tungsten probes on a two-probe setup at the temperature range of 100K to 300K. A special air-tight load lock suitcase was used to transfer the LiTiS\textsubscript{2}(en) device from the glovebox to the probe station. All electrical measurements were carried out under high vacuum (<5 × 10\textsuperscript{-5} torr).

3.3 Structural changes after Li intercalation

TiS\textsubscript{2}(en) was prepared by the 220 °C solvothermal reaction of TiCl\textsubscript{4}, elemental S, and en, and subsequently purified and crystallized in isopropanol. Pure TiS\textsubscript{2}(en) forms a unit cell with R-3c symmetry (room temperature: \(a = 18.596(1) \ \text{Å}, \ c = 9.0158(1) \ \text{Å}\)).
narrow full width half maximum (FWHM) (0.0014(3) radians for the (110) reflection) in the powder X-ray diffraction (XRD) pattern is indicative of its large (> 500 nm) crystalline domain size. For intercalation, the TiS$_2$(en) product was dispersed in hexane (dried using molecular sieves prior to use) in a glovebox, and stoichiometric equivalents of n-butyl Lithium ($n$-BuLi) dissolved in hexane were added to the mixture. The reaction mixture was sealed, removed from the glovebox and reacted at 50 °C for 1-2 days, and then the final product was collected via centrifugation and purified with hexane. The final product is extremely air and water-sensitive and all subsequent analyses were performed under inert Ar atmospheres.

After Li intercalation, the R-3c unit cell was still observed in the XRD pattern, however there was a noticeable shift in most of the observed reflections to lower $2\theta$ values (Figure 3.1 (b), (c)). The unit cell parameters, determined via a LeBail analysis, showed a large expansion (~0.6 Å) in the $a$ and $b$ direction and a slight contraction (~0.07 Å) in $c$ direction after reaction with one full equivalent of $n$-BuLi (Table 3.1). The expansion or contraction in the unit cell parameters is proportional to the number of equivalents of Li in the lattice (Figure 3.1 (d)). Additionally, after Li incorporation the FWHM of the diffraction peaks increases (0.0030(3) radians for the (110) reflection). The Williamson-Hall plot was prepared by using un-intercalated TiS$_2$(en) as standard. The FWHM of five most intense peaks ((110), (300), (211), 220), (420)) in the XRD patterns of LiTiS$_2$(en) and Li$_{0.66}$TiS$_2$(en) were measured and compared. The strong correlation between FWHM broadening and $2\theta$ is indicative of lattice strain as deduced via Williamson-Hall plot (Figure 3.2). Furthermore the strain increases with increasing Li intercalation.
stoichiometry. The Li: Ti ratios were further verified with Inductively Coupled Plasma-Optical Emission Spectroscopy measurements.

**Figure 3.1** (a) Crystal structures of TiS$_2$(en) (left) and LiTiS$_2$(en) (right) projected down the $c$ axis. (b)(c) X-ray diffraction patterns of TiS$_2$(en)(black), Li$_{0.66}$TiS$_2$(en)(red) and LiTiS$_2$(en). (d) Changes of unit cell parameter ($a$: black, $c$: red) with respect to Li/Ti ratio. (e) Crystal structures showing two adjacent 1D chains along $c$ axis with intercalated Li atoms positions determined from neutron diffraction refinements. Atom colors: Ti, red; S, yellow; N, green; C, black. H atoms have been omitted for clarity.
Table 3.1 LeBail analysis results of synchrotron XRD patterns of TiS$_2$(en) and LiTiS$_2$(en) at 100K

<table>
<thead>
<tr>
<th>Li/Ti</th>
<th>a (Å)</th>
<th>c (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>18.596(1)</td>
<td>9.015(5)</td>
</tr>
<tr>
<td>0.33</td>
<td>18.690(5)</td>
<td>9.009(1)</td>
</tr>
<tr>
<td>0.66</td>
<td>18.937(2)</td>
<td>9.004(1)</td>
</tr>
<tr>
<td>1.02</td>
<td>19.164(5)</td>
<td>8.949(4)</td>
</tr>
</tbody>
</table>

Figure 3.2 Williamson-Hall plot of Li$_{0.66}$TiS$_2$(en) and LiTiS$_2$(en) using TiS$_2$(en) as standard
Table 3.2 Bond lengths and bond valences of TiS$_2$(en) and LiTiS$_2$(en)

<table>
<thead>
<tr>
<th></th>
<th>TiS$_2$(en)</th>
<th>LiTiS$_2$(en)</th>
<th>Bond length (Å)</th>
<th>Bond Valence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-N</td>
<td>2.2788(17)</td>
<td>2.230(7)</td>
<td>0.394</td>
<td>0.354</td>
</tr>
<tr>
<td>Ti-S1</td>
<td>2.32763(26)</td>
<td>2.409(5)</td>
<td>0.817</td>
<td>0.656</td>
</tr>
<tr>
<td>Ti-S2</td>
<td>2.3564(25)</td>
<td>2.494(5)</td>
<td>0.756</td>
<td>0.521</td>
</tr>
<tr>
<td>Ti$^{n+}$</td>
<td>3.934</td>
<td></td>
<td></td>
<td>3.062</td>
</tr>
</tbody>
</table>

To elucidate the structure and the Li atom positions we used separate synchrotron and neutron diffraction measurements. Rietveld refinement of the synchrotron data shows that upon intercalation the inter-chain spacing increases from 6.151 Å to 6.380 Å, suggesting Li intercalation between the chains (Figure 3.3). The reduction in the $c$ parameter occurs due to the increased tilting of Ti octahedra. Furthermore, upon Li intercalation the Ti-S and Ti-N bond distances increase by $\sim$0.11 Å and $\sim$0.03 Å, respectively (Table 3.2). The bond valence sum of Ti in TiS$_2$(en) and LiTiS$_2$(en) are 3.93 and 3.10$^{49}$, respectively, further confirming the reduction of the Ti. To determine the positions of the Li atoms we did Rietveld refinement from Time-of-flight neutron diffraction measurements (Figure 3.4, Table 3.3). Li refines to the van der Waals gap between neighboring chains, and is
coordinated by three S atoms (Figure 3.1 (e)). The Li-S distances of 2.227(6) Å and 2.231(1) Å. The bond valence sum of Li in LiTiS$_2$(en) is 1.31, which suggests that Li has a +1 oxidation state. Other neutron and synchrotron refinement results for TiS$_2$(en) and LiTiS$_2$(en) are shown in Figure 3.5-3.7 and Table 3.4-3.5.

Figure 3.3 Inter-chain expansion after Li intercalation
Figure 3.4 TOF Neutron diffraction pattern Rietveld refinement of LiTiS$_2$(en) at 2K.

Table 3.3 GSAS refinement results for neutron diffraction of LiTiS$_2$(en) at 2K

<table>
<thead>
<tr>
<th>Phase</th>
<th>LiTiS2(en)$_{2K}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>LiTiS$_2$C$_2$H$_8$N$_2$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>179.06</td>
</tr>
<tr>
<td>Unit cell formula units Z</td>
<td>18</td>
</tr>
<tr>
<td>Space group</td>
<td>R-3c</td>
</tr>
<tr>
<td>a (Å)</td>
<td>18.5199(27)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>8.9328(19)</td>
</tr>
<tr>
<td>Unit cell volume V (Å$^3$)</td>
<td>2653.4(9)</td>
</tr>
<tr>
<td>$R_{wp}$</td>
<td>0.2387</td>
</tr>
<tr>
<td>$R_p$</td>
<td>0.3099</td>
</tr>
</tbody>
</table>
Figure 3.5 TOF Neutron diffraction pattern Rietveld refinement of TiS$_2$(en) at 2K.
Figure 3.6 Synchrotron XRD Rietveld refinement of TiS$_2$(en) at 100K.

Figure 3.7 Synchrotron XRD Rietveld refinement of LiTiS$_2$(en) at 100K.
Table 3.4 GSAS refinement results for neutron diffraction of TiS$_2$(en) at 2K

<table>
<thead>
<tr>
<th></th>
<th>TiS2(en)$_{2K}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase</td>
<td>TiS2(en)$_{2K}$</td>
</tr>
<tr>
<td>Chemical formula</td>
<td>C2H8N2S2Ti</td>
</tr>
<tr>
<td>Formula weight</td>
<td>172.12</td>
</tr>
<tr>
<td>Unit cell formula units Z</td>
<td>18</td>
</tr>
<tr>
<td>Space group</td>
<td>R-3c</td>
</tr>
<tr>
<td>a (Å)</td>
<td>18.3842(15)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>8.9121(19)</td>
</tr>
<tr>
<td>Unit cell volume V (Å$^3$)</td>
<td>2608.56(34)</td>
</tr>
<tr>
<td>$R_{wp}$</td>
<td>0.2664</td>
</tr>
<tr>
<td>$R_p$</td>
<td>0.3387</td>
</tr>
</tbody>
</table>
### Table 3.5 GSAS refinement results for synchrotron XRD patterns of TiS$_2$(en) and LiTiS$_2$(en) at 100K

<table>
<thead>
<tr>
<th>Empirical formula</th>
<th>C2H8N2S2Ti</th>
<th>LiC2H8N2S2Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fw</td>
<td>172.11</td>
<td>179.05</td>
</tr>
<tr>
<td>Space group</td>
<td>R-3c</td>
<td>R-3c</td>
</tr>
<tr>
<td>T (K)</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>a (Å)</td>
<td>18.5965(12)</td>
<td>19.1649(18)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>9.0139(11)</td>
<td>8.9400(13)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>2653.41(5)</td>
<td>2805.8(7)</td>
</tr>
<tr>
<td>λ (Å)</td>
<td>0.413248</td>
<td>0.413248</td>
</tr>
<tr>
<td>ρ (g cm⁻³)</td>
<td>1.84794(3)</td>
<td>1.8954(5)</td>
</tr>
<tr>
<td>Rwp</td>
<td>0.0795</td>
<td>0.0587</td>
</tr>
<tr>
<td>Rp</td>
<td>0.0597</td>
<td>0.0454</td>
</tr>
</tbody>
</table>
3.4 Probing reversibility by XRD and XPS

The Li$^+$ ions can be further deintercalated while preserving the structure by oxidizing the lattice. As prepared LiTiS$_2$(en) was dispersed in a THF solvent with stoichiometric equivalents of I$_2$ to oxidize the lattice. The product was then repeated washed in THF to remove the LiI. The XRD data for samples before and after intercalation and after deintercalation is shown in Figure 3.8 (a). The structure and lattice parameters of the sample after deintercalation are the same as the original TiS$_2$(en), confirming the reversibility of intercalation.

![Figure 3.8](image_url)

**Figure 3.8** (a) shift of peaks in the X-ray diffraction patterns. (b) changes of binding energy of Ti during reversible Li intercalation. (c) changes of Li peaks during reversible Li intercalation. Black: TiS$_2$(en), green: Li intercalated TiS$_2$(en), blue: deintercalated TiS$_2$(en).
X-ray photoelectron spectroscopy (XPS) was used to determine if Ti\(^{4+}\) is reduced to Ti\(^{3+}\) upon intercalation. In TiS\(_2\)(en) Ti, S, C, and N peaks were observed, but, upon intercalation, only the Ti peak energies were significantly changed. Figure 2b shows the changes in Ti peaks upon intercalation and deintercalation. TiS\(_2\)(en) has Ti 2p\(_{1/2}\) and 2p\(_{3/2}\) peaks occur at 464.0 eV and 458.2 eV, which is indicative of a Ti\(^{4+}\) oxidation state\(^{50-51}\). Additionally there is a small shoulder at 456.0 eV indicative of reduced Ti states. We suspect that this is due to some surface S atomic desorption in the ultra-high vacuum environment. Ar ion etching could not produce a clean stoichiometric surface and instead all of the peaks in the XPS spectrum were broadened after etching. Upon Li intercalation, the Ti peaks shift by \(~0.7\) eV, which is indicative of a change in oxidation state to Ti\(^{3+}\)\(^{52}\). Furthermore, the Ti 3s peak that originally occurs at 61.5 eV, is shifted to 60.0 eV upon Li intercalation\(^{53}\), along with the appearance of a Li 1s peak at 54.5 eV\(^{54}\) (Figure 3.8 (c)). This is relatively close to the reported binding energy of Li\(^+\) in Li\(_2\)S\(^{55-56}\). After treatment with I\(_2\)/THF the Ti peaks shift back to the energies observed in TiS\(_2\)(en), and the Li 1s peak almost completely disappears. The Li residual in the structure is estimated to be 7.4% after comparing the Li XPS peak areas before and after deintercalation. This confirms that the Ti\(^{4+}\) ion is indeed reduced to Ti\(^{3+}\) upon Li intercalation. The XPS survey spectra of the sample before and after the intercalation and deintercalation are shown in Figure 3.9-3.11.
Figure 3.9 XPS survey spectra of TiS$_2$(en)

Figure 3.10 XPS survey spectra of Li intercalated TiS$_2$(en)
Figure 3.11 XPS survey spectra of deintercalated LiTiS$_2$(en)

3.5 Thin film device and electrical conductivity

TiS$_2$(en) is a 1.7 eV direct band gap semiconductor. Upon Li intercalation, one would expect the conduction band to start filling, resulting in a significantly enhanced carrier concentration and lower resistivity values. In order to probe changes in electrical conductivity upon Lithium intercalation, we prepared two-probe current-voltage (IV) measurements of ~5 µm thick films of TiS$_2$(en) on glass substrates (Figure 3.12 (a)). Top-contact metal electrodes consisting of 650 nm of Ti and 20 nm of Au and separated by 10 µm lengths were defined by electron beam evaporation through a shadow mask (Figure 3.12 (b)).
Figure 3.12 (a) Simplified illustration of the thin film device (not drawn to scale). (b) Optical microscope image of one TiS$_2$(en) thin film device; insert: electron scanning microscope image of two contacts on the thin film. (c) IV curves of TiS$_2$(en) and LiTiS$_2$(en) in dark and Ar atmosphere. (d) IV curves of LiTiS$_2$(en) at different temperature; insert: resistivity vs. temperature plot.

The average two-probe resistivity of at least ten TiS$_2$(en) was measured to be $\sim$2.6 x $10^7$ $\Omega\cdot$cm (Figure 3.12 (c)). Then the device was placed in excess n-BuLi hexane solution for 1 day, rinsed with hexane and the conductivity was remeasured using the same contact pads, in order to minimize deviations due to variations in film thickness and particle-
particle contacts. Upon Li intercalation, the resistivity decreased by greater than one order of magnitude to $2.1 \times 10^6 \, \Omega \cdot \text{cm}$ (Figure 3.12 (c)). A 12-15-fold decrease in resistivity was observed for four different regions on the same film. This decrease in resistivity upon Li intercalation is most likely due to the enhanced carrier concentration upon doping. The resistivity of LiTiS$_2$(en) still increases upon cooling, indicative of semiconducting behavior (Figure 3.12 (d)). It is important to point out that the resistivity values measured from this 2-probe approach represent an upper bound of the material’s resistivity, since they neglect the influence of contact resistances that are evident from the non-ohmicity of the IV curves.

3.6 Conclusion

In summary, we have successfully shown that it is possible to reversibly intercalate up to one full equivalent of lithium inside this dimensionally-reduced hybrid organic/inorganic 1D lattice of TiS$_2$(en). Upon Li intercalation, the Ti$^{4+}$ is reduced to Ti$^{3+}$, and the conductivity of TiS$_2$(en) increase by at least an order of magnitude. The ability to tune the electron count of hybrid organic/inorganic dimensionally-reduced systems provides a pathway for the emergence of new physical phenomena, and could potentially impact existing technologies such as charge storage applications. For example, one could now explore how molecular-scale dimensionality affects the voltage, kinetics, and capacity of Li ion storage, comparing TiS$_2$ and TiS$_2$(en) as model electrode materials. More generally, we foresee the ability to intercalate different kinds of atoms into dimensionally reduced materials to be a powerful strategy to yield fundamentally new behavior.
References


Chapter 4  Solution phase synthesis of 2D vanadium chalcogenides and low temperature precursor phases

4.1 Introduction

The vanadium chalcogenide family contains a large number of binary and ternary metal chalcogenide solid state phases,\(^1\) as well as a large number of cluster phases.\(^2\) Due to the existence of the partially filled d-orbitals in these phases, they often exhibit novel magnetic behavior and correlated phenomena, such as charge density waves (CDW). At this CDW state, ionic lattice distorts due to the localized electrostatic interaction of electrons on neighboring atoms, creating a periodic “standing wave” like pattern. VS\(_2\) shows CDW state below 305 K,\(^3\) and VSe\(_2\) shows two CDW phases below 110 K and 80 K.\(^4\) Not only in bulk 2D phases, these phenomena are also prevalent at low dimensions. The transition temperature of VSe\(_2\) decreases with decreasing layer thickness.\(^5\) BaVS\(_3\) contains 1D chains of face-sharing V-S octahedra and it shows a metal-to-insulator and CDW transition at 70 K, and an incommensurate antiferromagnetic transition at 30 K.\(^6\) BaVSe\(_3\), on the other hand, shows a paramagnetic metal-ferromagnetic metal transition at 43 K.\(^7\) In the 1D corner-sharing chain of previously discussed LiTiS\(_2\)(en), which also contains d electrons along the chain, no the correlated phenomena can be observed. This may be due to the structural disorder on account of Li intercalation and the difference in

---

the polyhedral connectivity. Although these vanadium chalcogenides are of fundamental interest to researchers, the creation of these phases often go through the traditional high temperature solid state synthetic route and there have been limited solution-phase synthetic reports on 2D intercalated phases.\textsuperscript{8-10} Therefore, we seek to establish a solution-phase facile methodology to synthesize vanadium chalcogenides.

This chapter focuses on our exploration in the solution-phase chemistry of low dimensional vanadium chalcogenides. First, in our attempts to synthesize novel dimensionally-reduced derivatives of vanadium chalcogenide lattices, we created the first V-S dicubane cluster in a one-step solvothermal reaction. Second, we have established general routes towards creating 2D intercalated VS\textsubscript{2} and VSe\textsubscript{2} phases and have identified a low-temperature V(en)\textsubscript{3}Se\textsubscript{3} precursor phase as a precursor phase that forms in the initial steps of the solvothermal pathway. The understanding of the synthetic conditions and precursor chemistry lays the foundation for the rational synthesis of new novel vanadium chalcogenide structures.

4.2 \textit{V}_7\textit{S}_8 dicubane cluster

Cubane-type clusters represent an important class of polynmetallic compounds. They usually contain one or more L\textsubscript{\textit{n}}M\textsubscript{4}E\textsubscript{4} cuboidal cores, where E is the main group element and L is the ligand that binds to a metal M, which can consist of one or multiple metal types.\textsuperscript{11-13} The inorganic M\textsubscript{4}E\textsubscript{4} cores exist as the active sites in some of the most common biological systems such as photosystem II (Mn\textsubscript{3}CaO\textsubscript{4}),\textsuperscript{14} iron-containing hydrogenase and photosystem I (Fe\textsubscript{4}S\textsubscript{4})\textsuperscript{15}. These cubane cores vary electronically and structurally, based on
the total valence electron count of the cluster. For the transition metal tetrametallic cluster \( L_nM_4E_4 \), electron-full, low spin compounds have a highly symmetrical inorganic \( M_4E_4 \) cuboidal core and long metal-metal distances, like \( \text{Cp}_4\text{Co}_4\text{S}_4 \) (72\( e^- \), or 18\( e^-/\text{Co} \))\(^{16} \) (\( \text{Cp} = \) cyplopentadienyl), \( \text{Fe}_4\text{S}_4(\text{CO})_{12} \) (72\( e^- \) or 18\( e^-/\text{Fe} \)). Other cubanes, such as \( (i-\text{PrCp})_4\text{Mo}_4\text{S}_4 \) (60\( e^- \), or 15\( e^-/\text{Mo} \))\(^{18} \) also have symmetrical \( M_4S_4 \) cores but shorter intermetallic distances that indicate the existence of metal-metal bonding. Less studied are electron deficient early transition metal cubane clusters like \( \text{Cp}_4\text{V}_4\text{S}_4 \) (56\( e^- \) or 14\( e^-/\text{V} \))\(^{19} \) and \( (\text{MeCp})_4\text{Ti}_4\text{S}_4 \) (52\( e^- \) or 13\( e^-/\text{Ti} \))\(^{20} \). They feature highly distorted \( M_4S_4 \) cores\(^{21} \), even shorter intermetallic distances and significant metal-metal bonding.

Double cubane structures are also prevalent in biological systems, as the enhanced electron delocalization can influence the redox levels. These dicubanes are featured in the electron-transfer \( \text{PN} \) cluster \( (\text{Fe}_8\text{S}_9) \) (144\( e^- \) or 18\( e^-/\text{Fe} \)), which is comprised of two \( \text{Fe}_4\text{S}_4 \) cubanes connected by one corner-sharing \( \mu_6-\text{S} \) and two other external bridging \( \mu_2-\text{S} \).\(^{22-23} \)

Similarly, in the catalytic cofactor cluster of the MoFe protein of nitrogenase, the \( \text{Fe}_4\text{S}_3\text{C} \) and \( \text{MoFe}_3\text{S}_3\text{C} \) cubanes are connected by an interstitial C atom as well as three other external \( \mu_2-\text{S} \).\(^{24-25} \) The crystal structure of the vanadium nitrogenase cluster has not yet been elucidated,\(^{26} \) however vanadium analogues of the \( \text{PN} \) cluster, such as \( \text{V}_2\text{Fe}_6\text{S}_9 \) (136\( e^- \) or 18\( e^-/\text{Fe} \) and 14\( e^-/\text{V} \)), have been synthesized.\(^{27-29} \) These dicubane clusters are not only ideal model systems for gaining insight into biocatalytic mechanisms, but can also feature novel magnetic properties.\(^{30-32} \) Still, very few dicubane systems have been prepared, and early transition metal dicubane structures have not yet been discovered.\(^2,33 \)
In our attempts to synthesize novel dimensionally-reduced derivatives of vanadium chalcogenide solid-state lattices, we created the first V-S dicubane cluster in a one-step solvothermal reaction. This cluster has a stoichiometry of $\text{V}_7\text{S}_8\text{Cl}_2(\text{en})_6^{4+}$ and is the first dicubane that consists entirely of an early transition metal species. Herein, we present the crystal structure, magnetic properties, redox properties, and electronic structural analysis of this compound.

4.2.1 Experimental section

$\text{VCl}_4$ and thiourea were used as V and S precursors. Reactions and purifications were performed under Ar. After dissolving 0.36 g thiourea in 10 mL of distilled ethylenediamine, 0.25 mL of $\text{VCl}_4$ dissolved in 0.75 mL chlorobenzene was injected into the solution. This black mixture was heated at 120 °C for 2 hours and then transferred into a 25 mL Parr reactor and heated at 160 °C for 5 days. The reaction product was washed with isopropanol 3 times, with ethylenediamine once, then with 3 more times with isopropanol and finally vacuum dried. Black crystals were obtained after purification.

Single crystal diffraction data was collected on a Nonius Kappa CCD diffractometer at 150 K using an Oxford Cryostream Cooler. Elemental analysis was collected at Galbraith lab using the combustion method. Elemental Analysis confirmed both the ligand stoichiometry 38.6 % (36.8 % theoretical) and the ratio of C:H:N 2.1:8.2:2.0 (2:8:2, theoretical). The magnetic susceptibility was collected using a Quantum Design MPMS SQUID magnetometer within the temperature range of 5–300 K with both zero-field cooled conditions under the effect of an applied field of 50 G. EPR data of the cluster
solution was collected using a Bruker EMXPlus spectrometer at room temperature at a frequency of 9.426 GHz, a modulation amplitude of 10 G and a microwave power of 25.18 mW. The spectrum was averaged over six scans. The absorption spectrum was collected using a freshly-prepared 0.1 mM NMF solution on a Lambda 950 spectrophotometer (Perkin-Elmer) from 250-1500 nm with 1 nm resolution. Cyclic voltammetry data was collected using a glassy carbon working electrode, carbon counter electrode and a Ag+/Ag reference electrode (0.55 V) that was standardized using a ferrocene/ferrocene-redox couple. Data was collected using a Gamry Reference 600 with 5-200 mV/s scan rate and 10 mV step size in a 1.0 mM NMF solution with 0.2 M tetrabutylammonium hexafluorophosphate electrolyte, and protected under Ar.

The geometry of the isolated cation was self-consistently optimized using both hybrid restricted open-shell Hartree-Fock (ROHF)/DFT and unrestricted Hartree-Fock (UHF)/DFT methods with the B3LYP exchange-correlation potential, and the polarized 6-31G(d,p) basis set as implemented in Q-Chem, while preserving the inversion center at the central V atom. Self-consistent field calculations of the Kohn-Sham molecular orbitals and their eigenvalues used a relaxed constraint algorithm for the initial guess and was converged using direct inversion of the iterative subspace within a wavefunction error of $10^{-6}$. Atomic contributions to the frontier orbitals, Mulliken charges on each V atom, and Mayer bond orders were read or calculated from the output file of the self-consistent calculation. Molecular orbitals were plotted on 95% confidence interval isosurfaces using VESTA.
4.2.2 Crystal structure and electron count

This corner-sharing \( V_7S_8 \) dicubane structure (Figure 4.1 (a)) was synthesized by the reaction of \( \text{VCl}_4 \) with thiourea in ethylenediamine (\( \text{en} \)) in a solvothermal vessel. Black crystals were obtained after 5 days of reaction at 160 °C, with an overall yield of 61%. The crystal structure was resolved by single crystal X-ray diffraction at 150 K.

Figure 4.1 (a) \( V_7S_8 \) core of the dicubane cluster with V-S bond lengths labeled. (b) \( V_7S_8\text{Cl}_2(\text{en})_8^{4+} \) cluster neglecting H and Cl\(^-\) counterions. Color: V, red; S, yellow; Cl, green; C, black; N, blue.
The dicubane salt has a chemical formula of \([\text{V}_7\text{S}_8\text{Cl}_2(\text{en})_8]\)\text{Cl}_4\) and crystallizes into a triclinic P-1 unit cell. The cluster contains a dicubane \(\text{V}_7\text{S}_8\) core, and the two distorted \(\text{V}_4\text{S}_4\) cubes are connected via a central corner-sharing \(\text{V}\) atom (\(\text{V}1\)). This atom sits at the inversion center of the unit cell and is bonded to six neighboring \(\text{S}\) atoms in a distorted octahedral geometry. The other six \(\text{V}\) atoms in both cubes are bonded to three \(\text{S}\) atoms each and also satisfy the octahedral geometry by ligand coordination with \(\text{en}\) and \(\text{Cl}\). \(\text{V}2\) is bonded by one \(\text{cis}\)-binding \(\text{en}\) ligand and one \(\text{Cl}\) atom. \(\text{V}3\) and \(\text{V}4\) are bonded by one \(\text{cis}\)-binding \(\text{en}\) ligand and also share a second \(\text{en}\) ligand. Each cluster has four \(\text{Cl}^-\) counterions, giving a cluster stoichiometry of \([\text{V}_7\text{S}_8\text{Cl}_2(\text{en})_8]^4^+\) (Figure 4.1 (b)).

This cluster has a valence electron count of 97\(e^-\) or 13.86 \(e^-/V\). Based on the electron count, 1 \(\text{V}\) atom should have a +4 oxidation state, and the other six \(\text{V}\) atoms should be +3. The central and peripheral \(\text{V}\)-\(\text{S}\) bond lengths vary in length. The three \(\text{V}-\text{S}\) bond lengths of \(\text{V}2\), \(\text{V}3\) and \(\text{V}4\) (2.296–2.326 Å) are similar to the \(\text{V}-\text{S}\) bond lengths in the \((\text{MeCp})_4\text{V}_4\text{S}_4\) cubane cluster (2.294 Å),\(^{20}\) but are significantly shorter than the six \(\text{V}-\text{S}\) bond lengths of \(\text{V}1\) (2.387–2.434 Å). The \(\text{V}-\text{V}\) intermetallic distances between \(\text{V}2\), \(\text{V}3\) and \(\text{V}4\) range from 2.753–2.885 Å, which are only slightly shorter than those in \((\text{MeCp})_4\text{V}_4\text{S}_4\) (2.868–2.884 Å). The average \(\text{S}-\text{V}-\text{S}\) bond angle between \(\text{V}2\)-\(\text{V}4\) is 75.1°, also just slightly smaller than 77.8° in \((\text{MeCp})_4\text{V}_4\text{S}_4\).\(^{20}\) It is known that this monocubane features significant \(\text{V}-\text{V}\) bonding. The geometric similarity between \(\text{V}2\), \(\text{V}3\) and \(\text{V}4\) in the dicubane presented here and the vanadium atoms in \((\text{MeCp})_4\text{V}_4\text{S}_4\) suggests \(\text{V}-\text{V}\) bonding is also present among the six peripheral \(\text{V}\) atoms in this dicubane. The distances between \(\text{V}1\) and \(\text{V}2\)–\(\text{V}4\), however,
are considerably larger (3.159–3.217 Å), making V1 more isolated from the six peripheral V atoms. In the solid-state, this cluster oxidizes slowly over the span of a few months when stored in air. This cluster is sparingly soluble in N-methyl formamide (NMF) up to ~1 mM, and decomposes rapidly in water.

4.2.3 SQUID and EPR measurements

To further understand the electron configuration of the cluster, the magnetic susceptibility was measured. The zero-field-cool curve showed paramagnetic behavior from 5-300 K with no obvious transition (Figure 2a). A Curie-Weiss fit of the data gave an effective Bohr magneton of 1.73 μB per formula unit, indicating one unpaired electron per cluster. The fit also deviated from paramagnetic behavior below 150K and gave a θ value of -7.69 K, suggesting a weak antiferromagnetic interaction, likely between neighboring clusters. Similar weak antiferromagnetic coupling has also been reported in other vanadium complexes and clusters.37 Considering that the cluster has an odd number of total valence electrons, the one unpaired electron resides alone on the highest occupied molecular orbital (HOMO). The EPR (Electron paramagnetic resonance) spectrum of the solvated cluster confirmed one unpaired electron per formula unit and is localized on a single vanadium center. One set of EPR peaks with a g value of 2.013 was observed, which is split into 8 peaks with a hyperfine coupling constant of 91.2 cm⁻¹. This indicates the electron is coupled to a single ⁵¹V atom, which has a nuclear spin of 7/2. The uneven intensity of the 8 peaks is commonly seen in other vanadium complexes and arises due to the anisotropy of the hyperfine coupling constants and slow tumbling rate of the cluster in solution.38-40
Figure 4.2 (a) Magnetic susceptibility plot and Curie-Weiss fit of the zero-field-cool data.

(b) EPR spectrum of the cluster in NMF.
4.2.4 DFT calculations

Density functional theory (DFT) calculations were performed on the gas phase \( V_7S_8Cl_2(\text{en})_8^{4+} \) cation to illustrate the electronic configuration of the cluster\(^{41-43} \). Geometry optimizations with hybrid restricted open-shell Hartree-Fock ROHF/DFT and with unrestricted Hartree-Fock UHF/DFT yielded structures which differ from each other, with UHF bond lengths deviating more from experimental values, independently of the basis sets (6-31G(d,p), VDZ\(^{44} \), VTZ\(^{44} \) and exchange-correlation functionals tested (B3LYP, B2PLYP) (Table 4.1). Under ROHF/DFT, the cation optimized to a structure in better agreement with experiment than UHF/DFT. For example, the average difference between the experimental V-V/V-S bond lengths and the ROHF-minimized versus UHF-minimized structures are 0.05 Å and 0.15 Å, respectively. Thus, the ROHF/DFT minimized geometry was used for subsequent self-consistent electronic structure calculations. Several recent DFT studies on other transition metal cubane structures also note similar deviations from experiment when energy-minimized. For example, the copper(I) iodide cubanes \([\text{Cu}_4X_4L_4]\) (X = Cl, Br, I; L = pyridine or amine-based derivatives) exhibit deviations from experimental Cu-Cu distances on the order of 0.2 Å during DFT structural optimization.\(^{45} \) In addition, when the Mn\(_4\)O\(_4\)L\(_6\) cubane clusters are energy-minimized using B3LYP/Lanl2dz, several of the Mn-O bonds change by over 0.1 Å.\(^{46} \) Given the additional challenge associated with using Hartree-Fock exchange on open-shell systems, especially those with transition metals\(^{47} \), the large distortions observed in the \( V_7S_8Cl_2(\text{en})_8^{4+} \) cation during UHF optimization may be attributable to spin-contamination from the Hartree-Fock component of the exchange energy in B3LYP, where the self-consistent step at each geometry point
contains orbitals which are not eigenfunctions of the total $\hat{S}^2$ operator, leading to an unphysical solution.\textsuperscript{48}

Table 4.1 Interatomic distances for between V and S atoms in the crystal structure of $[\text{V}_7\text{S}_8\text{Cl}_2(\text{en})_8]\text{Cl}_4$ and in the $[\text{V}_7\text{S}_8\text{Cl}_2(\text{en})_8]^{4+}$ cation, optimized within the ROHF and UHF formalisms with the 6-31G(d,p) basis set and the B3LYP exchange-correlation potential.

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Crystal</th>
<th>ROHF</th>
<th>UHF</th>
</tr>
</thead>
<tbody>
<tr>
<td>V1-S1</td>
<td>2.421</td>
<td>2.457</td>
<td>2.519</td>
</tr>
<tr>
<td>V1-S2</td>
<td>2.387</td>
<td>2.426</td>
<td>2.452</td>
</tr>
<tr>
<td>V1-S3</td>
<td>2.434</td>
<td>2.459</td>
<td>2.514</td>
</tr>
<tr>
<td>V2-S2</td>
<td>2.296</td>
<td>2.325</td>
<td>2.434</td>
</tr>
<tr>
<td>V2-S3</td>
<td>2.311</td>
<td>2.305</td>
<td>2.481</td>
</tr>
<tr>
<td>V2-S4</td>
<td>2.326</td>
<td>2.415</td>
<td>2.488</td>
</tr>
<tr>
<td>V3-S1</td>
<td>2.304</td>
<td>2.301</td>
<td>2.324</td>
</tr>
<tr>
<td>V3-S2</td>
<td>2.311</td>
<td>2.298</td>
<td>2.350</td>
</tr>
<tr>
<td>V3-S4</td>
<td>2.319</td>
<td>2.303</td>
<td>2.356</td>
</tr>
<tr>
<td>V4-S1</td>
<td>2.296</td>
<td>2.266</td>
<td>2.401</td>
</tr>
<tr>
<td>V4-S3</td>
<td>2.318</td>
<td>2.285</td>
<td>2.378</td>
</tr>
<tr>
<td>V4-S4</td>
<td>2.314</td>
<td>2.296</td>
<td>2.339</td>
</tr>
<tr>
<td>V1-V2</td>
<td>3.190</td>
<td>3.376</td>
<td>3.509</td>
</tr>
<tr>
<td>V1-V3</td>
<td>3.159</td>
<td>3.135</td>
<td>3.345</td>
</tr>
<tr>
<td>V1-V4</td>
<td>3.217</td>
<td>3.084</td>
<td>3.419</td>
</tr>
<tr>
<td>V2-V3</td>
<td>2.815</td>
<td>2.734</td>
<td>3.144</td>
</tr>
<tr>
<td>V2-V4</td>
<td>2.885</td>
<td>2.912</td>
<td>3.306</td>
</tr>
<tr>
<td>V3-V4</td>
<td>2.753</td>
<td>2.585</td>
<td>3.005</td>
</tr>
</tbody>
</table>
Figure 4.3 Energy level (right) and Molecular orbital isosurfaces (left) for the $V_7S_8Cl_2(en)_8^{4+}$ cation from spin-unrestricted hybrid Hartree Fock/Density Functional Theory calculations (95% probability isosurfaces). The SOMO is outlined in blue and features localization at the central vanadium atom.
Figure 4.4 Zoomed in Molecular orbital isosurfaces for the $V_7S_8Cl_2(en)_8^{4+}$ cation from spin-unrestricted hybrid Hartree Fock/Density Functional Theory calculations (95% probability isosurfaces) for the 7 highest $\alpha$-spin SOMOs.
Table 4.2 MBOs between V and S atoms in the \([V_7S_8\text{Cl}_2(\text{en})_8]\)\(^{4+}\) cation, including ROHF and UHF calculations on experimental and ROHF-relaxed structures.

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Expt. ROHF</th>
<th>Expt. UHF</th>
<th>Relaxed ROHF</th>
<th>Relaxed UHF</th>
</tr>
</thead>
<tbody>
<tr>
<td>V1-S1</td>
<td>0.381</td>
<td>0.278</td>
<td>0.377</td>
<td>0.318</td>
</tr>
<tr>
<td>V1-S2</td>
<td>0.444</td>
<td>0.378</td>
<td>0.400</td>
<td>0.306</td>
</tr>
<tr>
<td>V1-S3</td>
<td>0.402</td>
<td>0.310</td>
<td>0.449</td>
<td>0.357</td>
</tr>
<tr>
<td>V2-S2</td>
<td>0.918</td>
<td>0.924</td>
<td>0.845</td>
<td>0.821</td>
</tr>
<tr>
<td>V2-S3</td>
<td>0.900</td>
<td>0.920</td>
<td>0.733</td>
<td>0.745</td>
</tr>
<tr>
<td>V2-S4</td>
<td>0.723</td>
<td>0.744</td>
<td>0.803</td>
<td>0.776</td>
</tr>
<tr>
<td>V3-S1</td>
<td>0.972</td>
<td>1.004</td>
<td>0.935</td>
<td>0.956</td>
</tr>
<tr>
<td>V3-S2</td>
<td>0.943</td>
<td>0.996</td>
<td>0.974</td>
<td>1.038</td>
</tr>
<tr>
<td>V3-S4</td>
<td>0.724</td>
<td>0.735</td>
<td>0.703</td>
<td>0.639</td>
</tr>
<tr>
<td>V4-S1</td>
<td>0.839</td>
<td>0.916</td>
<td>1.007</td>
<td>0.942</td>
</tr>
<tr>
<td>V4-S3</td>
<td>0.877</td>
<td>0.955</td>
<td>1.045</td>
<td>1.073</td>
</tr>
<tr>
<td>V4-S4</td>
<td>0.774</td>
<td>0.760</td>
<td>0.711</td>
<td>0.710</td>
</tr>
<tr>
<td>V1-V2</td>
<td>0.236</td>
<td>0.198</td>
<td>0.184</td>
<td>0.074</td>
</tr>
<tr>
<td>V1-V3</td>
<td>0.333</td>
<td>0.324</td>
<td>0.254</td>
<td>0.221</td>
</tr>
<tr>
<td>V1-V4</td>
<td>0.273</td>
<td>0.179</td>
<td>0.243</td>
<td>0.171</td>
</tr>
<tr>
<td>V2-V3</td>
<td>0.870</td>
<td>0.720</td>
<td>0.944</td>
<td>0.865</td>
</tr>
<tr>
<td>V2-V4</td>
<td>0.515</td>
<td>0.545</td>
<td>0.612</td>
<td>0.560</td>
</tr>
<tr>
<td>V3-V4</td>
<td>0.852</td>
<td>0.852</td>
<td>1.113</td>
<td>0.991</td>
</tr>
</tbody>
</table>
Table 4.3 Comparison of MBOs calculated in this work with those previously reported for metal-metal and metal-sulfur bonds in vanadium sulfide clusters. The V atoms in $[\text{V}_7\text{S}_8\text{Cl}_2(\text{en})_8]^{4+}$ are categorized into the central V$_c$ and the six peripheral V$_p$ atoms.

<table>
<thead>
<tr>
<th>V-S cluster</th>
<th>Bond</th>
<th>Average d / Å</th>
<th>Average MBO</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{V}_7\text{S}_8\text{Cl}_2(\text{en})_8]^{4+}$</td>
<td>V$_p$-V$_c$</td>
<td>3.198</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>V$_p$-V$_p$</td>
<td>2.744</td>
<td>0.80</td>
</tr>
<tr>
<td></td>
<td>V$_c$-S</td>
<td>2.447</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>V$_p$-S</td>
<td>2.310</td>
<td>0.86</td>
</tr>
<tr>
<td>$[\text{V}^{\text{III}}\text{O(tmm)}_2(\text{bipy})_2\text{Cl}]$</td>
<td>V-V</td>
<td>3.073</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>V-S</td>
<td>2.338</td>
<td>0.71</td>
</tr>
<tr>
<td>(HNEt$_3$)$_2[\text{V}^{\text{III}}\text{O(tmm)}_4]$</td>
<td>V-V</td>
<td>3.401</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>V-S</td>
<td>2.352</td>
<td>0.84</td>
</tr>
</tbody>
</table>
Using the optimized coordinates from ROHF/DFT, the spin-unrestricted molecular orbital (MO) diagram was calculated for the complex, and molecular orbitals in the frontier region are plotted in Figure 4.3 and Figure 4.4. According to these calculations, there are seven spin up electrons (α) and six spin-down electrons (β) giving an overall spin ½ cluster. The corresponding α-spin wavefunctions for the 7 highest singly-occupied molecular
orbitals (SOMO) are illustrated alongside the orbital energies. These SOMOs have significant contributions from d-orbitals on the peripheral V atoms. In the second to seventh highest SOMOs there is appreciable d-orbital overlap between the peripheral V2, V3, and V4 vanadium atoms, giving rise to calculated Mayer bond orders (MBO)\textsuperscript{49} of 0.87, 0.56 and 0.99 for V2-V3, V2-V4 and V3-V4, respectively (Table 4.2). These values are significantly higher than previously reported MBO values (0.12-0.14) of V-S clusters that lack V-V bonding (Table 4.3).\textsuperscript{50} In contrast, there is minimal orbital overlap between the peripheral vanadium atoms and the central vanadium atom, with calculated MBOs of 0.07, 0.22, and 0.17 for V1-V2, V1-V3, and V1-V4. However, it is important to point out that the calculated V2-V3, and V3-V4 distances are shorter than the experimental bond lengths by 0.08 and 0.17 Å, while the calculated V2-V4 bond distance is 0.03 Å longer. To assess the extent to which geometry optimization changes the bonding situation, Mayer bond orders (MBOs) were also calculated using the experimental structure for comparison. Again, a UHF self-consistent calculations gave rise to MBO values of 0.72, 0.55 and 0.85 for V2-V3, V2-V4 and V3-V4, respectively (Table 4.2). MBO values were also calculated from ROHF self-consistent calculations. In both the experimental structure, and minimized structure, and using both ROHF and UHF self-consistent calculations, the MBO values between pairs of peripheral V atoms are consistently above 0.5 and a factor of 3 higher than between the central V1 and peripheral V atoms. Therefore, no matter the choice of formalism, there is appreciable V-V bonding among the peripheral V atoms and little to the central V. Further confirming the validity of the obtained eigenvalues, at energies well below the vicinity of the SOMO (below -16 eV) the unrestricted MOs take on a pseudo-
closed shell character with an average splitting between $\alpha$ and $\beta$ levels to be within 30 meV (Figure 4.5). Additionally, the average difference in UHF and ROHF energies is 36 meV. The highest SOMO (outlined in blue) is derived almost entirely from d-orbitals on the central vanadium atom with negligible contributions from its neighbors. These findings are consistent with a single unpaired spin on one vanadium atom in the ground state, as determined from the magnetic susceptibility and EPR measurements.

4.2.5 Absorption and cyclic voltammetry

Finally, we characterized both the absorption and the redox properties of this cluster dissolved in NMF. A solubility test of this cluster in more than 30 different solvents was performed and NMF was the only solvent that showed a limited solubility of $\sim$ 1mM. An anion exchange reaction using AgPF$_6$ and AgBF$_4$ in NMF was also performed to increase the solubility of the cluster but it provided very little improvement. Therefore, the absorption and cyclic voltammetry measurements were conducted with saturated NMF solutions to acquire maximum signal from the cluster. The extinction coefficient of the cluster was calculated based on the ultraviolet-visible-near infrared absorption spectrum of a freshly prepared cluster solution (Figure 4.6 (a)). The onset of absorption started below 1500 nm with increased absorption at smaller wavelengths. Four broad peaks could be identified at 738, 528, 450 and 379 nm. The magnitude of the molar extinction coefficients (2000-5000 mol$^{-1}$Lcm$^{-1}$) as well as the energies at which these absorption processes occur (1.6-3.3 eV) indicate that they arise from d-d transitions. However, because of the large number of closely-related molecular orbitals in the frontier region, it is impossible to
simply assign these absorption peaks to specific transitions from the MO diagram. Due to
the water sensitivity of the cluster, the absorption spectrum changed drastically upon
exposure to atmosphere, and none of the original absorption peaks were observed after 30
min.

**Figure 4.6** (a) Extinction coefficient vs. wavelength plot calculated from the absorption
spectrum in NMF. (b) Cyclic voltammetry plot of the dicubane cluster solution in NMF,
showing 1 reduction and 4 oxidation waves. The open circuit voltage occurs at -0.35 V.

Also, the redox activity of the cluster was investigated using cyclic voltammetry
measurements, as shown in Figure S3b. The open-circuit voltage was measured to be -0.35
V vs. NHE. At a scan rate of 25 mV/s, four oxidation waves could be assigned, centered at
-0.25, +0.24, +0.66 and +0.97 V, respectively, with one reduction wave at -0.70 V as well.
The ΔE of the oxidation and reduction peaks (~120 mV) and the difference in the oxidation
and reduction peak current both indicate the irreversible nature of the redox processes in NMF. Therefore, the number of electrons involved within these processes could not be identified. The same irreversible nature is observed at scan rates varying from 5-200 mV/s, indicating decomposition of the cluster.

4.3 2D vanadium chalcogenides and low temperature precursor phases

The synthesis of 2D vanadium chalcogenides traditionally requires high temperature annealing over a long period of time. Recently, solution-phase synthesis methods have been developed for creating metal chalcogenide nanocrystals and nanosheets. These methods often utilize chalcogenide precursors like S-amine complex,\textsuperscript{51} chalcogen-thio-amine mixture,\textsuperscript{52} thioacetamide,\textsuperscript{9} diorganyl dichalcogenides.\textsuperscript{53} In particular, for vanadium sulfide synthesis, Na\textsubscript{3}VO\textsubscript{4} and thioacetamide are used as precursors, and vanadium is reduced by HS\textsuperscript{9}. For vanadium selenide synthesis, NH\textsubscript{3}VO\textsubscript{3} and SeO\textsubscript{2} are co-reduced by HCOOH.\textsuperscript{10} Herein, we developed a general method to synthesize amine intercalated VS\textsubscript{2} and VSe\textsubscript{2} without redox chemistry, using molecular precursor VCl\textsubscript{4} and chalcogen-amine complex under solvothermal conditions. The low temperature precursor phases of these reactions have also been identified, providing more information on the reaction mechanism. While the choices of different chalcogen precursors and amines will not have much effect on the creation of 2D intercalated phases, they will influence the formation of the low temperature precursor phases.
4.3.1 Experimental section

VCl₄ and S powder were used as V and S precursors. Reactions and purifications were performed under Ar. After dissolving 0.32 g S in 10 mL of distilled ethylenediamine or other amines, 0.5 mL of VCl₄ dissolved in 0.3 mL chlorobenzene was injected into the solution. This black mixture was heated at 120 °C for 2 hours and then transferred into a 25 mL Parr reactor and heated at various temperature for 5 days. The reaction product was washed with isopropanol 3 times, with ethylenediamine once, then with 3 more times with isopropanol and finally vacuum dried. Powders were obtained after purification.

Similarly, for V-Se systems, VCl₄ and Se powder were used as V and Se precursors. In the V:Se = 1:2 reaction, 0.80 g Se was dissolved in 10 mL of distilled ethylenediamine or other amines by heating the mixture at 170 °C for 1h, then 0.5 mL of VCl₄ dissolved in 0.3 mL chlorobenzene was injected into the solution. This black mixture was heated at 120 °C for 2 hours and then transferred into a 25 mL Parr reactor and heated at various temperature for 5 days. The reaction product was washed with ethylenediamine 3 times, then 3 more times with isopropanol and methanol and finally vacuum dried. In an alternative method, Se powder was dissolved in ethylenediamine first by adding half equivalent amount of NaBH₄ (Se:NaBH₄ = 2:1) before adding VCl₄.

X-ray diffraction patterns were collected on powder samples using a Rigaku Miniflex powder diffractometer (30 kV, 15 mA, Cu X-ray tube, 293K). Diffraction data was also collected using a Bruker D8 powder diffractometer (40 kV, 50 mA, sealed Cu X-ray tube).
The magnetic susceptibility was collected using a Quantum Design MPMS SQUID magnetometer within the temperature range of 5–300 K with both zero-field cooled conditions under the effect of an applied field of 50 G.

4.3.2 Vanadium sulfide system at different temperatures

The reactions of VCl$_4$ and S powder in different primary amines were studied extensively. During the reaction, the primary amine first serves as a sacrificial agent to reduce the S powder to the S$^{2-}$ state, as well as serving as a ligand and a solvent, similar to its role in the synthesis of the 1D titanium chalcogenide derivatives. Thioacetamide can also be used as an alternative S precursor, due to the fact that upon heating it will decompose to give H$_2$S. Reactions using both S precursors will yield identical results.

The XRD patterns of the products of the reactions in en at 120 - 200 °C are shown in Figure 4.7. Similar to the results of the titanium sulfide system, at high temperatures (above 160 °C), the dominating phase is the 2D intercalated VS$_2$. The first two most intense peaks around 9 degrees and 18 degrees are the (003) and (006) of the 2D phase. At low temperature region (below 120 °C), while the 2D phase is still present, there is a new phase emerging that matches the pattern of the previously synthesized V$_7$S$_8$ dicubane cluster. This cluster phase can be considered as the low temperature precursor phase to the more stable 2D phase. Given the fact that the ratio of S:V in V$_7$S$_8$ is much smaller than that in VS$_2$, and the majority of the V atoms are reduced from 4+ to 3+, the formation of this precursor phase is likely due to the incomplete dissociation of the active S precursor thioamide and its potential redox reaction with VCl$_4$. 

125
Figure 4.7 XRD patterns of products from VCl$_4$ and S powder reactions in en at different temperatures.

Reactions utilizing $pn$ as the ligand yielded similar results. Instead of have a low temperature precursor phase, the 2D intercalated VS$_2$ phase is even more stable over the entire range of 120 to 200 °C, with narrower peak FWHM and better crystallinity at higher synthesis temperature (Figure 4.8). Similar results can be observed for reactions with
different monodentate primary amines (C3-C8). An example of the reactions with octylamine (oa) is shown in Figure 4.9. In all of these trials, no dimensionally reduced derivatives or low temperature precursor phases can be isolated. This indicates that for V atom, the ligand binding affinity of pn or all the monodentate amines are too small to prevent the V-S bonds from forming.

Figure 4.8 XRD patterns of products from VCl₄ and S powder reactions in pn at different temperatures.
Figure 4.9 XRD patterns of products from VCl₄ and S powder reactions in *oa* at different temperatures.

4.3.3 Vanadium selenide system at different temperatures

Analogous to the vanadium sulfide system, Se powder and *en* were used as the Se precursor. However, at room temperature, Se powder does not react with amines. In order to create a selenoamide active species, the mixture of Se and *en* was first heated for 1 hour at 170 °C, resulting in a black solution before adding VCl₄ into the mixture.⁵²,⁵⁴
Comparing the results of the vanadium selenide to the sulfide system, not surprising, the higher temperature region (above 160 °C) is again predominately the 2D VSe$_2$ phase, as shown in Figure 4.10. In the XRD pattern of the 2D structure, the first peak below 10 degrees two theta corresponds to the (003) peak of the intercalated phase. The next weak peak around 17.5 degrees is the (006) peak. The peak around 26 degrees is the (009) peaks. At lower temperature, below 120 °C, the 2D phase is not observable and there exists a completely new phase according to XRD. This product was phase pure and this new phase was indexed to have a space group of C2/c and a monoclinic unit cell of 11.50948(97)Å, 15.0063(13)Å, 9.27083(70)Å and $\beta=89.9544(81)^\circ$. The reaction at 100 °C gave identical
results to the 120 °C reaction. Below 100 °C, the crystallinity of the product decreased and the product became amorphous.

![Crystal structure of the low-temperature precursor phase VSe$_3$(en)$_3$.](image)

**Figure 4.11** Crystal structure of the low-temperature precursor phase VSe$_3$(en)$_3$.

Elemental analysis of the 120 °C reaction product showed that V:Se:C:H:N = 1:3.2:6.4:25.2:6.3 (theoretical 1:3:6:24:6), which gave the empirical formula of VSe$_3$(en)$_3$. Rietveld refinement on the powder diffraction pattern generated the structure shown in **Figure 4.11**. In this structure, no V-Se bond has been formed. The unit cell was composed of alternating tri(ethylenediamine)vanadium complex cations and triselenide anions. In previous reports, there have been some structures that contain polychalcogenide anions (X$_3^{2-}$, X$_5^{2-}$, X$_7^{2-}$), but they are usually bonded to the metal. The triselenide anion shows a
bent structure and the Se-Se bond distance is 2.369 Å and the Se-Se-Se bond angle is 102.4°, very close to the values in the previously reported structures. The vanadium is coordinated by three ethylenediamine molecules in a slightly distorted octahedral geometry which forms a chiral complex with lambda or delta conformation. The V-N bond distances as well as the C-C and N-N bond distances are within the agreeable range of previously reported structures but due to poor ability of the light atoms to scatter X-ray, some of the peak intensity of the pattern cannot be fit perfectly, especially when using the lab X-ray diffractometer.

Figure 4.12 Rietveld refinement of VSe$_3$(en)$_3$ lab X-ray powder pattern.
Table 4.4 Rietveld refinement results of VSe$_3$(en)$_3$

<table>
<thead>
<tr>
<th>Empirical formula</th>
<th>VSe$_3$C$_6$N$_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_w$</td>
<td>443.93</td>
</tr>
<tr>
<td>Space Group</td>
<td>C2/c</td>
</tr>
<tr>
<td>a (Å)</td>
<td>11.50948(97)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>15.0063(13)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>9.27083(70)</td>
</tr>
<tr>
<td>beta</td>
<td>89.9544(81)</td>
</tr>
<tr>
<td>Cell Volume (Å$^3$)</td>
<td>1601.21(23)</td>
</tr>
<tr>
<td>T (K)</td>
<td>295</td>
</tr>
<tr>
<td>λ (Å)</td>
<td>1.5406</td>
</tr>
<tr>
<td>pattern range (2θ, °)</td>
<td>5-60</td>
</tr>
<tr>
<td>$R_{wp}$</td>
<td>0.1106</td>
</tr>
</tbody>
</table>

Figure 4.13 ZFC plot of VSe$_3$(en)$_3$ and the Curie-Weiss fit.

132
The +2 oxidation state of the V atom lead to a d³ electron configuration, resulting in 3 unpaired electrons per formula unit. This information was confirmed by the SQUID measurement. The ZFC and FC curves of the sample were identical, both showing an increasing magnetic susceptibility with decreasing temperature (Figure 4.13). The 1/χ vs. T was also plotted on the same graph and the linear trend indicated the paramagnetic nature of the sample, with a small deviation at the lower temperature region. The Curie-Weiss fit of the data points above 150 K gave a θ value of -9.2 K, indicating a small antiferromagnetic interaction and the effective Bohr magneton µ_eff = 3.59, very close to the value of 3.87 of 3 unpaired electrons without any spin-orbit coupling.

Similar to the vanadium sulfide system, at low temperature, we were able to identify a coordination complex phase as a low temperature precursor phase to the 2D phase. In this cluster, the cation is a tris(ethylenediamine) vanadium(II) complex. This is a confirmation of the earlier proposed mechanism in Chapter 2 that for these types of solution phase synthesis reactions the metal amine complexes forms first before the formation of metal chalcogen bonds. The formation of the Se₃²⁻ anion is also an indication that this cluster is the precursor phase towards the 2D vanadium selenide phase. The Se is not fully reduced to Se²⁻ at 120 °C this temperature, giving rise to the polychalcogenide. This kind of behavior has been widely observed in the synthesis of chalcogenides and chalcogenidometalates in amines at relatively lower temperature.  S powder and amines can directly react at room temperature and form reduced polysulfides and thioamides. At temperature as low as 130 °C, thioamides become the main species and it will decompose to give H₂S. However, for Se the solvation process only occurs after the Se-amine mixture
heated, and polyselenides are the initial reduced species. Only at elevated temperature (above 160 °C), the organoselenides start to form and decompose to give H₂Se.\textsuperscript{52, 58} This confirms the results that Se\textsubscript{3}\textsuperscript{2-} forms at lower temperature while Se\textsuperscript{2-} forms that high temperature.

![XRD patterns](image)

**Figure 4.14** XRD patterns of products from VCl₄ and Se and NaBH₄ reactions in en at different temperatures. Starred peaks are from impurities.

An alternative route to deliver Se\textsuperscript{2-} is to use a stronger reducing agent to convert Se powder to Se\textsuperscript{2-} first in amine solution and in this way both vanadium and selenium are in

134
the desired oxidation states before the reaction of the two. NaBH$_4$ was used as the reducing agent and the 2:1 ratio of Se:NaBH$_4$ should yield completely reduced Se$^{2-}$. **Figure 4.13** showed the results of some of the reactions by this method. The critical temperature at which the 2D phase forms dropped down to 140 °C from 160 °C, underlining the enhanced reactivity of the new Se precursor at lower temperature region. Below 120 °C, a new phase that is different from the previously mentioned cluster phase appeared. After eliminating some of the impurity peaks (marked by star in the XRD pattern), this new phase was indexed to have a monoclinic unit cell (P2$_1$/n, $a = 14.1555$ Å, $b = 10.9977$ Å, $c = 6.5876$ Å, $\beta = 94.273^\circ$). Further experiments will need to be performed to elucidate the crystal structure of this compound.

### 4.4 Conclusion

We studied the precursor chemistry, ligand affinity and synthetic temperature of various vanadium sulfide and vanadium selenide phases. The inorganic 2D vanadium chalcogenide phases are prevalent at higher temperature region and even more stable when the ligand has a relatively smaller binding affinity towards the metal. At lower temperatures, in both the V-S and V-Se systems, cluster or coordination complex precursor phases can be observed. These precursor phases represent the intermediates between the molecular precursors and the final 2D extended lattices. One of the clusters, V$_7$S$_8$Cl$_2$(en)$_8$$^{4+}$, represents the first example of an early transition metal dicubane cluster. DFT, EPR, magnetic susceptibility, and analysis of the crystal structure all suggest that this structure-type consists of 6 peripheral V$^{3+}$ atoms distorted from octahedral geometry with significant
metal-metal bonding and a central corner-sharing V$^{4+}$ atom joining the two cubes. While this corner-shared cube motif is well-represented in solid-state systems, particularly spinel-type lattices such as CuV$_2$S$_4$, as well as in bioinorganic proteins, synthetic dicubanes are rare in molecular systems. Considering the prevalence of this motif in biological electron transfer processes, further control of the ligand, chalcogen atom, and metal oxidation states may enable the preparation of new synthetic dicubane analogues with enhanced stability, solubility and catalytic activity.

References


31. Triki, S.; Thetiot, F.; Pala, J. S.; Golhen, S.; Clemente-Juan, J. M.; Gomez-Garcia, C. J.; Coronado, E. Heptanuclear hydroxo-bridged copper cluster of the dicubane-like type: structural and magnetic characterisations of [Cu$_7$(OH)$_6$Cl$_2$(pn)$_6$(H$_2$O)$_2$](C(CN)$_3$)$_4$Cl$_2$ (pn = 1,3-diaminopropane). *Chem. Commun.* **2001**, *2172-2173.


Brooks, B. R.; Chan, G. K. L.; Chipman, D. M.; Cramer, C. J.; Goddard, W. A.; Gordon,
M. S.; Hohre, W. J.; Klamt, A.; Schaefer, H. F.; Schmidt, M. W.; Sherrill, C. D.; Truhlar,
D. G.; Warshel, A.; Xu, X.; Aspuru-Guzik, A.; Baer, R.; Bell, A. T.; Besley, N. A.; Chai,
Kong, J.; Lambrecht, D. S.; Liang, W.; Ochsenfeld, C.; Rassolov, V. A.; Slipchenko, L.
V.; Subotnik, J. E.; Van Voorhis, T.; Herbert, J. M.; Krylov, A. I.; Gill, P. M. W.; Head-
Gordon, M. Advances in molecular quantum chemistry contained in the Q-Chem 4

44. Schäfer, A.; Horn, H.; Ahlrichs, R. Fully optimized contracted Gaussian basis sets

J.-Y.; Gacoin, T.; Boilot, J.-P. Thermochromic Luminescence of Copper Iodide Clusters:

46. Kuznetsov, A. E.; Geletii, Y. V.; Hill, C. L.; Musaev, D. G. Insights into the


48. Menon, A. S.; Radom, L. Consequences of Spin Contamination in Unrestricted
Calculations on Open-Shell Species: Effect of Hartree–Fock and Møller–Plesset


Chapter 5  Conclusion

Just as nanoscience transformed our conventional understanding of the physical behavior of materials, there is no doubt that taking this concept to its physical limits, to atomic-scale materials, will lead to exciting new discoveries. While a handful of these atomic-scale lattices have now been prepared, we are only starting to understand how to rationally create a specific derivative of a particular solid-state structure. Further insight into how the precursor chemistry, organic structure, and binding-type can enable the formation of different derivatives, will help transform the synthesis of these systems from discovery to design.

Using titanium chalcogenides and vanadium chalcogenides as model systems, various atomic scale derivatives and clusters are created and the synthetic conditions for these new phases and the 2D metal chalcogenide phases are explored. A general synthetic method was developed using metal halides and chalcogen-amine complex as molecular precursors. Primary amines were used as the solvent as well as the ligand to inhibit the propagation of the inorganic lattice. In the titanium sulfide system, the synthetic phase diagrams were constructed for the 1D chain derivatives of TiS$_2$(en) and TiS$_2$(pn). These atomic scale derivatives are thermodynamically stable at relatively lower temperature and high ligand to metal ratio. However, even a small change to the ligand from en to pn, the region where the 1D phase can be accessed is changed significantly, due to the difference in binding affinity of the ligand. The selenide and oxyselenide analogues of the 1D structure can also
be created. Compared to the original 2D VS\textsubscript{2} and VSe\textsubscript{2}, which is an indirect band gap semiconductor and a semimetal respectively, the 1D derivatives shift from indirect to direct band gap, and have increased band gap due to quantum confinement. The magnitude of the increment in the band gap energy is similar in the sulfide and selenide systems.

The Li intercalation process in these 1D van der Waals derivatives was studied using TiS\textsubscript{2}(en). The structural changes and the reversible nature of the intercalation were monitored using synchrotron and neutron diffraction and XPS. Upon Li intercalation, the Li atoms reside in the van der Waals gaps between the chains and the Ti is reduced from 4+ to 3+ and the conductivity increases more than 10 fold after one equivalent of Li is intercalated.

Similar to the titanium chalcogenide systems, the synthetic phase space of the vanadium chalcogenides were extensive explored. The 2D VS\textsubscript{2} and VSe\textsubscript{2} phases are more easily accessed over a wider range of temperature and again is the prevalent at higher temperature region. Unlike the 1D chain derivatives, the low temperature phases of the vanadium chalcogenides consist of various clusters rather than extended 1D lattices. One of the clusters, V\textsubscript{7}S\textsubscript{8}(en)\textsubscript{8}Cl\textsubscript{6}, has a unique corner-sharing dicubane structure. This cluster is electron deficient and possesses only one unpaired electron per formula unit, which is confirmed by SQUID and EPR measurements and DFT calculations. The vanadium selenide low temperature phase, VSe\textsubscript{3}(en)\textsubscript{3}, is composed of V(en)\textsubscript{3}\textsuperscript{2+} cation and Se\textsubscript{3}\textsuperscript{2-} anion and has no V-Se bonding. These new structures at low temperature are considered to be the intermediates or the precursor phases between the molecular precursors and the 2D phases. The results in the vanadium chalcogenide systems elucidate the reaction pathways
from molecules to extended lattices and at the same time underline the rich chemistry in cluster formation at lower temperature region.

Overall, the studies discussed above aim to establish a general synthetic methodology and construct a roadmap to rationally create the atomic scale derivatives and clusters of the transition metal chalcogenides. Compared with the parent 2D metal chalcogenide lattices, the structural changes, electronic and optoelectronic and magnetic properties of these stable chemical systems are carefully investigated. These efforts help us systematically understand how certain derivatives can be created and how their structural change influence band structures, intercalation chemistry and magnetic behavior, leading to a step further towards the rational design and synthesize functional materials for optoelectronics, charge storage and catalysis applications.
Chapter 1


60. Kamihara, Y.; Watanabe, T.; Hirano, M.; Hosono, H. Iron-Based Layered Superconductor \(\text{La}[\text{O}_{1-x}\text{F}_x]\text{FeAs} (x = 0.05–0.12)\) with \(T_c = 26\) K. *J. Am. Chem. Soc.* **2008**, 130, 3296-3297.


80. Cahill, D. G.; Braun, P. V.; Chen, G.; Clarke, D. R.; Fan, S.; Goodson, K. E.; Keblinski, P.; King, W. P.; Mahan, G. D.; Majumdar, A.; Maris, H. J.; Phillpot, S. R.; Pop,


Chapter 2


**Chapter 3**


Chapter 4


42. Momma, K.; Izumi, F. VESTA 3 for three-dimensional visualization of crystal, 

Lange, A. W.; Behn, A.; Deng, J.; Feng, X.; Ghosh, D.; Goldey, M.; Horn, P. R.; Jacobson, 
M.; Richard, R. M.; Rohrdanz, M. A.; Steele, R. P.; Sundstrom, E. J.; Woodcock, H. L.; 
Zimmerman, P. M.; Zuev, D.; Albrecht, B.; Alguire, E.; Austin, B.; Beran, G. J. O.; 
Chang, C.-M.; Chen, Y.; Chien, S. H.; Closser, K. D.; Crittenden, D. L.; Diedenhofen, M.; 
DiStasio, R. A.; Do, H.; Dutoi, A. D.; Edgar, R. G.; Fatehi, S.; Fusti-Molnar, L.; Ghysels, 
A.; Golubeva-Zadorozhnaya, A.; Gomes, J.; Hanson-Heine, M. W. D.; Harbach, P. H. P.; 
T.; Krauter, C. M.; Lao, K. U.; Laurent, A. D.; Lawler, K. V.; Levchenko, S. V.; Lin, C. 
Y.; Liu, F.; Livshits, E.; Lochan, R. C.; Luenser, A.; Manohar, P.; Manzer, S. F.; Mao, S.- 
P.; Mardirossian, N.; Marenich, A. V.; Maurer, S. A.; Mayhall, N. J.; Neuscamman, E.; 
Oana, C. M.; Olivares-Amaya, R.; O’Neill, D. P.; Parkhill, J. A.; Perrine, T. M.; Peverati, 
R.; Prociuk, A.; Rehn, D. R.; Rosta, E.; Russ, N. J.; Sharada, S. M.; Sharma, S.; Small, D. 
W.; Sodt, A.; Stein, T.; Stück, D.; Su, Y.-C.; Thom, A. J. W.; Tsuchimochi, T.; Vanovschi, 


Appendix: Rights and Permissions


**Figure 1.5**: Reprinted with permission from Losego, M. D.; Blitz, I. P.; Vaia, R. A.; Cahill, D. G.; Braun, P. V. Ultralow Thermal Conductivity in Organoclay Nanolaminates Synthesized via Simple Self-Assembly. *Nano Lett.* **2013**, *13*, 2215-2219. Copyright 2013 American Chemical Society.


