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# PREPARATION OF METAL THIOLATE COMPLEXES

# FOR CONTROLLED SYNTHESIS OF NANOMATERIALS

Βy

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iv

List	of Figures	. vi
List	of Schemes	. viii
List	of Tables	. x
Abst	tract	. xi
1.0	Introduction	. 1
1.1	Background, Literature Precedent, & Previous Work	. 5
1.2	Experimental Techniques	. 27
2.0	Experimental	. 30
2.1	First Attempts to Prepare Zinc Thiolate Materials	. 31
2.2	Current Methods for Synthesizing Zinc Thiolate Materials	. 33
2.3	Current Methods for Synthesizing Tin Thiolate Materials	. 34
2.4	Gold Precursors and Materials	. 34
2.5	Attempts to Prepare AuIn SSPs	. 37
2.6	Thermolysis Studies and Precursors	. 38
3.0	Results and Discussion	. 41
3.1	Preparation and Characterization of Gold Precursors	. 41
3.2	Use of Gold Precursors in Nanocrystal Synthesis	. 51
3.3	First Attempts to Prepare Zinc Thiolate Complexes	. 57
3.4	Current Methods for Synthesizing Zinc Thiolate Complexes	. 63
3.5	Current Methods for Synthesizing Tin Thiolate Complexes	. 66
4.0	Conclusion	. 69
5.0	References	. 72

# TABLE OF CONTENTS

# LIST OF FIGURES

Figure 1	Unit cells of (a) chalcopyrite and (b) sphalerite material7	
Figure 2	ORETP diagram of $(Ph_3P)_2Ag(\mu-SEt)_2Ga(t-SEt)_2$ in solid state 1	1
Figure 3	Room temperature <sup>1</sup> H NMR spectrum of <b>5</b> in CD <sub>2</sub> Cl <sub>2</sub> 1	4
Figure 4	<sup>1</sup> H NMR spectra of <b>5</b> in CD <sub>2</sub> Cl <sub>2</sub> at variable temperatures	5
Figure 5	<sup>1</sup> H NMR spectra of <b>2</b> in CD <sub>2</sub> Cl <sub>2</sub> at variable temperatures 1	6
Figure 6	XRD spectra of varying ratios of nanocrystals <b>a - g</b> depicting the	
differing phas	es2	0
Figure 7	Solid state UV-Vis data of nanocrystals NC-3/6 a – g 2	1
Figure 8	Unit cells of (a) stannite and (b) kesterite2	3
Figure 9	<sup>1</sup> H NMR spectrum of PPh <sub>3</sub> AuGa(SEt) <sub>4</sub> (18) 4	4
Figure 10	Low temperature <sup>1</sup> H NMR spectra of PPh <sub>3</sub> AuGa(SEt) <sub>4</sub> (18) 4	5
Figure 11	TGA trace of PPh <sub>3</sub> AuGa(SEt) <sub>4</sub> (18)4	5
Figure 12	<sup>1</sup> H NMR spectrum of AuGa(SAr) <sub>4</sub> (20)4	8
Figure 13	TGA trace of (PPh <sub>3</sub> )AuGa(SAr) <sub>4</sub> (20)4	.9
Figure 14	XRD spectra of nanocrystals <b>NC-5/18 a – g</b> 5	3
Figure 15	XRD spectra of nanocrystals <b>NC-5/20 a – d</b> 5	4
Figure 16	Solid state UV-Vis spectra of NC-5/18 a - g and NC-5/20 a - d 5	5
Figure 17	Spectrum of <b>9</b> at room temperature and 70 <sup>o</sup> C6	2
Figure 18	<sup>1</sup> H NMR spectrum of (TMEDA)Zn(SEt) <sub>2</sub> (14)6	4
Figure 19	<sup>1</sup> H NMR spectrum of (IM) <sub>2</sub> Zn(SEt) <sub>2</sub> (15)6	5
Figure 20	Potential strategies for CZTS nanomaterials via the SSP	
approach		7

Figure 21	<sup>1</sup> H NMR spectrum of Sn(SEt) <sub>4</sub> ( <b>16</b> )	
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### LIST OF SCHEMES

Scheme 1	Two general approaches to producing I-III-IV (MES <sub>2</sub> ) chalcopyrite
nanomaterial	s2
Scheme 2	General synthesis for I-III-IV SSP materials
Scheme 3	General synthesis of doped nanocrystals 3
Scheme 4	The synthesis of SSP (PPh <sub>3</sub> ) <sub>2</sub> CuIn(QR) <sub>4</sub> 9
Scheme 5	The synthesis of metal thiocarboxylates and production of metal
sulfide nanoc	rystals10
Scheme 6	Solution phase decomposition of SSPs <b>3</b> and <b>6</b> to produce alloyed
nanocrystals	<b>NC-3/6 a-g</b>
Scheme 7	Synthesis of soluble zinc-bis(thiolate) complexes of
1-methylimidi	zole
Scheme 8	Synthesis of zinc-bis(dodecanethiolate)25
Scheme 9	a) Preparation of gem-di(iodozincio)methane species. b) General
process of So	chlenk equilibrium for production of diiodozinc species
Scheme 10	Preparation of (PhS) <sub>4</sub> Sn26
Scheme 11	First attempts to produce (PPh <sub>3</sub> )AuGa(SEt) <sub>4</sub> 41
Scheme 12	Synthesis of (PPh <sub>3</sub> )AuGa(SEt) <sub>4</sub> ( <b>18</b> )43
Scheme 13	Synthesis of (PPh <sub>3</sub> )AuGa(SAr) <sub>4</sub> precursor ( <b>20</b> ) via ligand
Exchange	
Scheme 14	Attempted synthesis of a AuIn SSP 50
Scheme 15	Attempted synthesis of a AuIn SSP 50

Scheme 16 Nanocrystal synthesis employing varying ratios of 18 and 20 to 5 to					
produce alloyed nanocrystals NC-5/18 a - g and NC-5/20 a – d					
Scheme 17	Acid-base route to zinc thiolates	59			
Scheme 18	Potential insoluble zinc polymeric structure	59			
Scheme 19	Possible synthetic route to produce soluble zinc thiolate				
compounds v	vith neutral ligands	61			
Scheme 20	Synthesis of soluble zinc thiolate complexes with neutral ligands				
TMEDA and	1-methylimidizole attached (14, 15)	63			
Scheme 21	Synthesis of soluble zinc dodecanethiolate (8)	66			

## LIST OF TABLES

Table 1	Structural parameters of $(Ph_3P)_2M(\mu-SEt)_2E(t-SEt)_2$ complexes in	
the solid state	е	12
Table 2	Summary of solution phase decomposition of nanocrystals	
NC-3/6 a – g		17
Table 3	Summary of XRD, UV-Vis and ICP-OES solution phase	
decompositio	on studies of nanocrystals <b>NC-3/6 a – g</b>	21
Table 4	Solution phase decomposition studies with ratios of <b>18</b> or <b>20</b> with <b>5</b>	
to produce al	lloyed nanocrystals NC-5/18 a - g and NC-5/20 a – d	53
Table 5	Characterization of nanocrystals NC-5/18 a - g and	
NC-5/20 a –	d	56
Table 6	Summary of polymeric zinc thiolates <b>10 – 13</b>	59

#### ABSTRACT

Metal sulfide nanocrystals are useful for their electronic and optical properties, especially in photovoltaic devices. Copper-indium-gallium-selenide (CIGS) is of particular interest due to its desirable band gap, and has been employed as the absorber layer in photovoltaic devices. A major drawback of this multicomponent material is the difficulty in synthesizing it with desired stoichiometries, phases, and particle sizes. One possible strategy to overcome this challenge is to synthesize these materials using single source precursors (SSPs, or "molecular precursors") which combine metals in predetermined stoichiometry and surround them with thiolate and ancillary ligands. Upon thermolysis, these precursors decompose to the respective metal sulfide nanocrystals.

This work tests the limits of this approach by combining known SSPs with bimetallic gold complexes and characterizing the fate of the gold in the resulting nanocrystals. Various ratios of Au/Ga and Cu/Ga molecular precursors were thermolyzed together, but no evidence of gold incorporation into chalcopyrite was observed by XRD, ICP-OES, or UV-Vis. Instead, metallic gold and CuGaS<sub>2</sub> were produced. This result is most readily explained by the fact that gold is easily reduced and is therefore difficult to incorporate within these materials as the (I) component of a I-III-VI chalcopyrite system.

Cu<sub>2</sub>ZnSnS<sub>4</sub> (CZTS) is another promising material for photovoltaics due to the relatively low cost and limited toxicity of its components, and another demanding test of the SSP approach because of its quaternary structure. Zinc

xi

and tin thiolate precursors have been prepared as a first step towards synthesizing SSPs for CZTS. Initial steps in the synthesis and characterization of these complexes are described.

#### **1.0 INTRODUCTION**

The efficient conversion of sunlight into useable energy has been among the highest priorities in energy research as long as the field has existed. The first generation of solar cells were based on crystalline silicon and were developed in 1954 at Bell Laboratories in Murray Hill, New Jersey.<sup>3</sup> These original devices were only 6% efficient, due largely to a 1.1 eV band gap offset from peak solar radiation at 1.35 eV.<sup>27</sup> Even though these devices had low efficiency, this discovery kicked off decades of research which not only improved upon siliconbased solar cells but also developed ideas for new thin films and ultimately nanocrystals.<sup>3</sup> Researchers expanded upon solar cells and sought new absorber materials with electronic properties similar to those of silicon. This led to CdS, PbS, and HgS semiconductor materials which boast tunable band gaps, an important property for semiconductors, but are composed of toxic elements.<sup>40</sup> Efforts to replace these toxic elements with alternatives of similar electronic properties led to ternary chalcopyrites of the type I-III-VI<sub>2</sub>, such as CuInS<sub>2</sub> and AqGaS<sub>2</sub>.<sup>27</sup> These materials are comparatively non-toxic, but include relatively rare elements. This in turn lead to the production of copper, zinc, tin sulfide (CZTS) materials which are composed with elements that are abundant and nontoxic. The complexity of these materials increases as they progress towards environmentally benign and affordable compositions, in turn increasing the difficulty of imposing the degree of stoichiometric control required for their syntheses. Therefore, methods for synthesizing these materials with controlled stoichiometry are of interest.

One main approach to synthesizing nanocrystalline chalcopyrites is through solvothermal synthesis. This can be conducted in one of two ways: a multiple-source approach or a single source precursor approach (SSP) (Scheme 1). The multiple source approach utilizes easily attainable precursors, but offers limited control of stoichiometry, the starting materials may have varying decomposition rates, volatilities, or decomposition temperatures, limiting the flexibility of viable reaction conditions. Instead of selectively producing the wanted MES<sub>2</sub> chalcopyrite material, unwanted byproducts of M<sub>2</sub>S or E<sub>2</sub>S<sub>3</sub> nanocrystals may also be produced. In contrast, the SSP approach involves one molecule that contains the appropriate ratios of M and E held together by thiolate and phosphine ligands so that upon thermolysis, the stoichiometry is



predetermined. This allows for wider flexibility of introducing dopants within the materials and otherwise tuning reaction conditions. The drawback to this approach is that the SSPs are time consuming and expensive to synthesize.

Scheme 1. Two general approaches to producing I-III-IV (MES<sub>2</sub>) chalcopyrite nanomaterials.

Previous work has described the synthesis of chalcopyrite SSPs and their characterization in solution and solid phases (Scheme 2).<sup>17</sup> In addition, SSPs

have been used successfully to prepare chalcopyrite materials containing dopants (Scheme 3). In these studies, various ratios of two different SSPs were thermalized together and the resulting nanocrystals were characterized by XRD to determine their phases, solid state UV-Vis to find band gap energies, and ICP-OES to establish elemental composition. In one study the III element in the I-III-VI<sub>2</sub> was varied between Ga and In by using varying ratios of (PPh<sub>3</sub>)<sub>2</sub>CuGa(SEt)<sub>4</sub> and (PPh<sub>3</sub>)<sub>2</sub>CuIn(SEt)<sub>4</sub>.<sup>17</sup> In a subsequent study, the identity of the I element in chalcopyrite was modulated by using varying ratios of (PPh<sub>3</sub>)<sub>2</sub>CuIn(SEt)<sub>4</sub> to (PPh<sub>3</sub>)<sub>2</sub>AgIn(SEt)<sub>4</sub>.<sup>35</sup> These studies showed the relative band gap energies varied depending on the elements within the material. In addition, the Ag:Cu



decomposition studies showed the phase of the material changed above a critical threshold of Ag composition. At lower concentrations of Ag, the chalcopyrite phase predominated and at higher Ag concentrations the wurtzite phase dominated (*vida infra*).

Scheme 2. General synthesis for I- M = Cu, Ag E = Al, Ga, In, Fe III-IV SSP materials.



Scheme 3. General synthesis of doped nanocrystals.

The research described below was designed to test the limits of the SSP method by continuing down group 11 to see if Au could also be incorporated within the chalcopyrite structure using similar approaches to produce nanocrystals Cu<sub>1-x</sub>Au<sub>x</sub>GaS<sub>2</sub>. Au (I) is difficult to incorporate as a dopant within chalcopyrite materials due to its susceptibility towards reduction and its preference toward linear coordination, as opposed to the tetrahedral coordination more common to Cu and Ag. In our research we wanted to prepare gold SSPs, perform thermolysis studies with various ratios of two different SSPs, and characterize the products to determine the fate of gold.

Our research also explored the value of SSPs by endeavoring to prepare appropriate precursors for quaternary CZTS nanocrystals. The benefit of CZTS nanocrystals is that while their properties are similar to those of CIGS, the elements used are relatively abundant, non-toxic, environmentally friendly, and cost efficient.<sup>26</sup> Within our work we were interested in producing soluble zinc and tin thiolate complexes for potential in synthesizing a ZnSn SSP for eventual production of CZTS nanocrystals.

In order to put my work in a meaningful context, this document will necessarily encompass previous research by co-workers exploring the SSP

approach to chalcopyrite nanocrystals, including SSP synthesis by Margulieux et al., solution characterization by Nguyen et al., and preparation of doped nanomaterials by Sun et al., and Adhikari et al.<sup>17, 33, 35</sup> Mashael Alharbi also contributed to preliminary efforts to prepare gold SSPs.<sup>36</sup> All subsequent gold work, as well as preliminary syntheses of zinc and tin thiolate complexes, represents my own contribution to this ongoing project.

### 1.1 BACKGROUND, LITERATURE PRECEDENT, & PREVIOUS WORK

#### **NANOPARTICLES AND CHALCOPYRITE**

Nanoparticles, also known as nanocrystals, are defined as ranging in size from 1 - 100 nm, and depending on its size, a given particle can exhibit a wide range of physical properties. For example, controlling the size changes melting point temperature and the peak absorption wavelength, which in turn depends on the band gap.<sup>5,7-8</sup> A band gap is defined as the difference in energy from the valence to the conduction band, analogous to the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in a discrete molecule. In order for electron promotion to the LUMO to occur, energy in the form of heat or light must be absorbed in an amount corresponding to the band gap of the system. If an electron can be excited from the HOMO to the LUMO by a useful wavelength, and the material possesses conductive properties, it may potentially be used for photovoltaic or other optical devices. If the band gap is too large, then the electron cannot

readily be promoted to the higher energy state LUMO and the material is therefore considered an insulator. Band gaps can be modified by introducing dopants with bands between the HOMO and LUMO into the material, allowing electron promotion to occur more readily. The band gap is measured in eV, where higher eV correlates to a larger band gap. Typical band gap values for semiconductor materials range from 0.1 to 4.0 eV and an insulator is typically above 4.0 eV; however, depending on the material these numbers can vary.<sup>24</sup> To be used for solar radiation absorption, a band gap of 1.35 eV is ideal.<sup>27</sup> In addition, eV is inversely related to wavelength and thus determines the color of light absorbed and emitted by the material. This can be seen in the equation E =  $hc/\lambda$  where *h* is Planck's constant (6.262 X 10<sup>-34</sup> Js) and *c* is the speed of light (2.99 X 10<sup>8</sup> m/s). To calculate the band gap energy from a spectroscopic absorption edge value in nm, this equation can be converted into appropriate units to the form eV = 1240 eV · nm/\lambda.

Among the materials that have semiconducting properties suitable for solar power applications are ternary metal sulfides in the chalcopyrite family. These have a general formula of I-III-IV<sub>2</sub> where I = Cu, Ag; II = AI, Ga, In; and IV = S, Se, Te.<sup>1,2,9</sup> Chalcopyrites have 8 atoms per unit cell where each cation is tetrahedrally bound to 4 anions and each anion is bound to 2 cations of 1<sup>+</sup> formal charge (also referred to as group 1 in this field) as well as 2 cations of 3<sup>+</sup> charge (group III) (Figure 1a).<sup>9,10</sup> Chalcopyrites are derivatives of the zincblende or sphalerite structure, in which the Zn (II) sites are replaced by a 50:50 mixture of M(I) and M(III) cations. The ZnS example adopts an interpenetrating face

centered cubic arrangement where each zinc is bound to 4 sulfur atoms and each sulfur is bound to 4 zinc atoms (Figure 1b).<sup>9</sup>



Figure 1. Unit cells of (a) chalcopyrite material and (b) sphalerite material.<sup>38</sup>

Chalcopyrite materials exhibit a wide range of chemical and physical properties, including band gaps, that can be further tuned by careful control of nanocrystal size and/or the introduction of dopants to make them useful materials for photovoltaic solar cells, light emitting diodes, and optical devices.<sup>9,11</sup> For example, Cu(In/Ga)S<sub>2</sub> has been utilized as an absorber layer in thin film solar cells due to its high stability and efficiency for power conversion.<sup>12</sup> Moon and coworkers showed CIGS materials have bifacial properties, meaning they can

absorb light from either side of the film. This has potential applications in solar powered windows where the sun or indoor light promotes conduction.<sup>12</sup> Chen and coworkers used CuInS<sub>2</sub> nanocrystals for applications in dye-sensitized solar cells where varied amounts of copper were added to In<sub>2</sub>S<sub>3</sub> nanoplates which tuned the band gap of CuInS<sub>2</sub> from 1.45 to 1.19 eV as Cu/In molar ratios increased from 0.7 to 2.9.<sup>13</sup> In addition, Castro and coworkers used thermolysis to decompose the precursor (PPh<sub>3</sub>)<sub>2</sub>CuIn(SEt)<sub>4</sub> to produce CuInS<sub>2</sub> nanocrystals. Their results showed the size of the nanocrystals could be changed from 2 to 4 nm by simply varying the temperature of the reaction from 200 <sup>o</sup> C to 250 <sup>o</sup> C.<sup>20</sup> These are just a few examples of the uses for chalcopyrite metal chalcogenide materials.

#### SYNTHESIZING CHALCOPYRITE

Optimizing methods to synthesize a wide variety of chalcopyrite and related materials to reliably control the phase, size, and stoichiometry of particles is still underway.<sup>14,15</sup> As mentioned previously, there are two general synthetic approaches for chalcopyrites: combination of multiple sources, and use of SSPs (Scheme 1).

In the multi-source approach, Reiss and coworkers synthesized CuInS<sub>2</sub> by mixing In(OAc)<sub>3</sub> and CuI in 1-dodecanethiol and 1-octadecene under an inert atmosphere.<sup>15</sup> The reaction was then heated to 200 <sup>0</sup> C for 40 minutes until the solution changed from colorless to dark brown. Park and Kim synthesized CuInS<sub>2</sub> chalcopyrite material using similar methodologies.<sup>14</sup> This approach utilizes three

separate, easily attainable precursors that decompose to produce nanocrystals of the desired ternary product. One main drawback of this methodology, however, is the difficulty in controlling the stoichiometry of the nanocrystal. This is caused by different decomposition rates, volatility, and reactivities of the sources used, limiting the flexibility to performing reactions at different temperatures or ratios of the starting material to accommodate other modifications to the chalcopyrite materials.<sup>16</sup> In contrast, the SSP approach can avoid this issue because it utilizes precursors that deliver the desired elements in the proper stoichiometry surrounded by supporting ligands. One stipulation for this approach is that when these precursors are decomposed, the bonds of the intended nanoparticle material need to be stronger than those to the supporting ligands.<sup>16</sup> The decomposition of these products occurs in solution phase via conventional thermolysis, microwave thermolysis, and photolysis.<sup>18-20</sup> Synthesizing these SSPs can be time consuming and expensive, however.

Hirpo and coworkers synthesized one of the first SSPs for chalcopyrites in 1993.<sup>22</sup> They were interested in producing CuInSe<sub>2</sub> or CuInS<sub>2</sub> chalcopyrite nanoparticles. Previously, Kazmerski synthesized these materials, but their methods required high temperatures reaching to 1300 <sup>o</sup> C.<sup>25</sup> To avoid these unfavorable conditions, Hirpo developed SSPs, (PPh<sub>3</sub>)<sub>2</sub>CuIn(QR)<sub>4</sub> (Q = S, Se, R = Et, <sup>i</sup>Bu), that decomposed to the respective nanoparticles at 330 <sup>o</sup> C (Scheme

 $InCl_{3} + 4KQR \longrightarrow K^{+} + [In(QR)_{4}]^{-} + 3KCI \quad (1)$   $[(Ph_{3}P)_{2}Cu(CH_{3}CN)_{2}]^{+} + [In(QR)_{4}]^{-} \longrightarrow (Ph_{3}P)_{2}CuIn(QR)_{4} + 2CH_{3}CN \quad (2)$  Q = S, Se  $R = Et, ^{i}Bu$ 

4).

Scheme 4. The synthesis of SSP (PPh<sub>3</sub>)<sub>2</sub>Culn(QR)<sub>4</sub>.

Another approach by Hampden-Smith and coworkers was to synthesize group 12 metal thiocarboxylate SSPs  $M(SOCR)_2L_2$  (M = Zn, Cd, R = alkyl, aryl, L = lewis base), and decompose them to their respective metal sulfide nano materi als throug  $[(RCOS)M-S-M(SOCR)]L_2 \rightarrow [(RCOS)M-S-M(SOCR)]L_2 + S(COR)_2(1)$ h a  $[(RCOS)M-S-M(SOCR)]L_2 \rightarrow 2MS + S(COR)_2 + 2L$  (2) h a M = Zn, Cd R = alkyl, arylthioca rboxylic anhydride elimination (Scheme 5).<sup>21</sup>

Scheme 5. The synthesis of metal thiocarboxylates and production of metal sulfide nanocrystals.

#### **CHARACTERIZATION OF SINGLE SOURCE PRECURSORS**

In a more recent method developed by Matthew Kihara and coworkers, one equivalent of MCI (M = Cu, Ag) is treated with 2 equivalents of PR<sub>3</sub> in benzene at ambient temperatures and inert conditions (Scheme 2).<sup>17</sup> 1 equivalent of ECI<sub>3</sub> (E = In, Ga, AI, Fe) is added to the solution and stirred at 60 - 80 ° C (reactions with M = Ag conducted at 60 ° C and M = Cu at 80 ° C). 4 equivalents of NaSR are added to the reaction and allowed to stir at the respective temperature. The resulting solution is filtered and the filtrate is evaporated to dryness and recrystallized. The resulting structures were determined by X-ray Diffraction (XRD) by Margulieux and coworkers and are illustrated in Figure 2 and summarized in Table 1.<sup>17</sup>



**Figure 2.** ORETP Diagram of  $(Ph_3P)_2Ag(\mu-SEt)_2Ga(t-SEt)_2$  in solid state.

M / E	Ag / Al 1	Ag / Ga 2	Ag / In 3	Cu / Al 4	Cu / Ga 5	Cu / In 6
M–P1	2.5030(6)	2.4497(7)	2.5017(6)	2.2894(7)	2.3010(8)	2.278(2)
M–P2	2.4508(5)	2.5025(8)	2.4523(5)	2.2782(7)	2.2693(8)	

M–S1	2.6185(6)	2.6159(8)	2.6247(6)	2.4013(6)	2.3800(8)	2.418(2)
M–S2	2.6824(5)	2.6829(8)	2.6847(6)	2.4172(8)	2.4527(9)	
<mark>Ε</mark> –(μ-S)	2.2892(7)	2.3192(8)	2.4959(6)	2.2702(11)	2.3159(8)	2.494(2)
E–(t-S)	2.2273(8)	2.2429(9)	2.4272(7)	2.2185(11)	2.2423(8)	2.419(3)

**Table 1.** Structural parameters of  $(Ph_3P)_2M(\mu-SEt)_2E(t-SEt)_2$  complexes in the solid state.

The SSPs **1** - **6** have similar structures with two thiolate bridging ligands between M and E and two terminal thiolate ligands on E. Significant differences between the structures were M–P, M–S, and E–S bond lengths and the ring geometries, which depend on the metals involved. In gereral, the Ag-P and Ag-S bonds were about 0.20 Å longer than the Cu–P and Cu–S bonds oweing to different sizes of the atomic radii. When comparing 1 - 3 with 4 - 6, the latter group adopts a planar CuS<sub>2</sub>E ring as compared to the puckered ring for AgS<sub>2</sub>E.These structures were also characterized by <sup>1</sup>H NMR to determine if the molecules have similar properties in the solution phase (Figure 3). At room temperature only one thiolate environment is observed. These results could mean there is a tight ion pair  $[(Ph_3P)_2M][E(SEt)_4]$  where no thiolate ligands are attached to M(I), or that the bridging and terminal thiolate ligands are exchanging too rapidly to be distinguished by NMR. To test between the two possibilities, low temperature <sup>1</sup>H NMR studies were conducted. If the bridging and terminal ligands are exchanging, then two separate environments for the thiolate ligands would be detected. At -95 ° C, 5 showed two separate thiolate environments of equal intensity corresponding to the bridging and terminal thiolate ligands, confirming

the rapid exchange hypothesis (Figure 4). Low temperature <sup>1</sup>H NMR studies conducted on **2** did not show separation of the thiolate signals (Figure 5). This result neither confirms nor disproves either potential hypothesis; it could mean the compound exists as a tight ion pair, or the exchange between the two ligands are occurring at a faster rate than **5** and thus be beyond detection by <sup>1</sup>H NMR.<sup>33</sup>



Figure 3. Room temperature <sup>1</sup>H NMR spectrum of 5 in CD<sub>2</sub>Cl<sub>2</sub>.<sup>33</sup>



Figure 4. <sup>1</sup>H NMR spectra of 5 in CD<sub>2</sub>Cl<sub>2</sub> at variable temperatures.<sup>33</sup>



Figure 5. <sup>1</sup>H NMR spectra of 2 in CD<sub>2</sub>Cl<sub>2</sub> at variable temperatures.<sup>33</sup>

### **DECOMPOSITION STUDIES**

Previous work by Adhikari and coworkers, explored solution phase decomposition studies of mixing two "SSPs" **3** and **6** in varied ratios to produce alloyed nanocrystals **NC-3/6 a - g** (This annotation denotes the two SSPs used for decomposition to the nanocrystal where the letters dictate the relative ratios of the two SSPs) (Scheme 6).<sup>35</sup> The resulting ratios are summarized in Table 2.



Scheme 6. Solution phase decomposition of SSPs 3 and 6 to produce alloyed

Mol % Culn SSP 6	Mol % AgIn SSP 3	NC-3/6
100	0	а
80	20	b
60	40	С
40	60	d
20	80	е
10	90	f
0	100	g

#### nanocrystals NC-3/6 a-g.

Table 2. Summary of solution phase decomposition of nanocrystals NC-3/6 a - g.

In this reaction, two separate molecular precursors are decomposed together to produce nanocrystals. (Note that since two separate precursors are used, "molecular precursor" is a more accurate term than SSP.) Complexes 3 and **6** were added together in varying ratios in benzyl acetate. 1,2 - ethanedithiol was added in excess, and the mixture was heated for 1 hour at 180 ° C. After collection and washing, the nanoparticles were characterized by X-ray diffraction (XRD) for crystal structure, inductively coupled plasma optical emission spectroscopy (ICP-OES) for elemental analysis, and solid state ultraviolet-visible spectroscopy (UV-Vis) for band gap determination. The XRD shows the changes in phase in the nanocrystals across varying compositions (Figure 6). From 0-60% of silver precursor **3**, the chalcopyrite phase predominates with peaks consistent to the tetragonal CuInS<sub>2</sub> reference pattern 85-1575 (JCPDS-03-065-2732) with major peaks at  $2\theta$  = 28.0, 46.4, and 55.0°. From 80-100% of **3**, the wurtzite phase is predominant, and the pattern is most consistent to reference JCPDS 19-0193. Across this range, the band gap ranged from 1.36 eV to 1.70 eV. (Figure 7 and Table 3). More specifically, from 0-60% of **3**, the chalcopyrite phase dominated, exhibiting a band gap range of 1.56 eV to 1.36 eV respectively. At 80% and 90% of **3**, the phase was a mixture of chalcopyrite and wurtzite with a band gap of 1.48 eV and 1.54 eV. Finally, at 100% of **3**, the wurtzite phase dominated with the largest band gap of 1.70 eV. These results show that depending on the ratio between 3 and 6, the phase of the nanocrystals could be modified selectively for targeted band gap energies with alloyed Ag/In chalcopyrite at lower concentrations of **3** to the wurtzite structure predominating

at higher concentrations. More importantly, the content and phase of the material could be adjusted in a controlled manner by simply changing the ratio of the precursor molecules. This allowed for Ag to adopt the chalcopyrite phase which it does not adopt in its pure form. ICP-OES data confirms the ratios of elements in the materials.



Figure 6. XRD spectra of varying ratios of nanocrystals NC-3/6 a - g depicting the differing phases.



Figure 7. Solid state UV-Vis data of nanocrystals NC-3/6 a - g.

NC-3/6	Phase	Band Gap (eV)	Ag% of M(I) ICP	(Cu+Ag)/In	(Cu+In+Ag)/S
а	Chalcopyrite	1.56	0	1.4	1.0
b	Chalcopyrite	1.20	14.3	1.2	1.1
С	Chalcopyrite	1.36	30.4	1.1	1.1
d	Chalcopyrite	1.37	59.9	1.0	1.0
е	Chalc./Wurt.	1.54	66.7	1.0	1.0
f	Chalc./Wurt.	1.48	76.9	1.0	1.0
g	Wurtzite	1.70	100	0.9	1.0

Table 3. Summary of XRD, UV-Vis and ICP-OES solution phase decomposition

studies of nanocrystals NC-3/6 a - g.

#### **GOLD RESEARCH**

Our research is designed to test the limits of the SSP method by seeing if Au (I) could also be incorporated within the chalcopyrite structure using similar approaches by producing a AuGa SSP and decomposing it with the respective CuGa SSP 5 for nanocrystal production. As explained previously, gold (I) is difficult to incorporate as a dopant within chalcopyrite materials due to its susceptibility towards reduction and its preference toward linear coordination. Looking at the electrochemical properties, Au has the lowest reductive potential of any metal, meaning it is susceptible to reduction or gaining an electron.<sup>23</sup> This means in an SSP molecule, Au (I) is more likely than Cu(I) or Ag (I) to undergo reduction upon thermolysis, which could produce metallic Au rather than Au (I) incorporation within the chalcopyrite structure. Looking at the electron configurations of group 11 elements in the +1 oxidation state, they all have a filled d<sup>10</sup> shell which explains the stability of Cu(I) and Ag(I) but doesn't explain why Au still prefers the metallic form. The main reason is that Au, a postlanthanide element, contains a much larger number of protons. This high nuclear charge has a disproportionately large impact on the attraction of s electrons that penetrate closest to the nucleus, which in turn results in their further relativistic stabilization, ultimately bringing s electrons closer to the nucleus causing shorter covalent bond lengths between Au and ligands.<sup>23</sup> Short bond distances increase the repulsive interactions of ligands both with each other and with valence d electrons, and this phenomenon explains why Au (I) prefers a linear geometry

while Cu (I) and Ag (I), which suffer less repulsion, both prefer a tetrahedral geometry. When preparing Au SSPs, these factors will need to be kept in mind.

### $CU_2ZNSNS_2$ (CZTS)

In addition, our research explored the value of SSPs by preparing appropriate zinc and tin thiolate precursors for quaternary Cu<sub>2</sub>ZnSnS<sub>2</sub> (CZTS) nanocrystals. CZTS can adopt either of two phases, kesterite and stannite, with the kesterite structure predominating as the more thermodynamically stable geometry.<sup>28</sup> The difference between the two tetragonal structures is a different arrangement of Cu and Zn atoms (Figure 8). CZTS has a bandgap about 1.40 to 1.50 eV which is close to the ideal bandgap of 1.35 eV for semiconductor solar cells.<sup>27-28</sup> Due to these factors, CZTS materials have potential to replace the CIGS absorber layer and its relatively rare and toxic components in thin films.



Figure 8. Unit cells of (a) stannite and (b) kesterite.<sup>31</sup>

Surprisingly, there are few well-characterized examples of soluble zinc thiolate complexes that might be starting points for the preparation of ZnCu or ZnSn precursors. Rees and coworkers were among the first to describe preparation of soluble metal-*bis*(thiolate) complexes with incorporation of a neutral ligand, 1-methylimidizole (Scheme 7).<sup>29</sup> In their reaction,  $Zn(SO_4) \cdot 7H_2O$ was dissolved in a 1:1 ratio of distilled water and ethanol. 25% ammonium hydroxide was added to dissolve any metal hydroxides in solution, and the desired alkyl thiol was added dropwise. The resulting zinc-*bis*(thiolate) compound, after collection and washing, was added to 1-methylimidizole in



toluene to produce an imidizole adduct of the zinc-*bis*(thiolate).

Scheme 7. Synthesis of soluble zinc-*bis*(thiolate) complexes of 1methylimidizole.

Antolini and coworkers slightly modified Rees' procedures to produce soluble zinc-*bis*(thiolate) compounds without further introduction of additional ligands such as 1-methylimidizole.  $Zn(NO_3)_2 \cdot 6H_2O$  is added to ethanol.<sup>34</sup> 25%
ammonium hydroxide is added until the metal hydroxide is completely dissolved. Dodecanethiol is added and the resulting white precipitate is collected via centrifugation and dried under vacuum (Scheme 8) The resulting zinc*bis*(dodecanethiolate) complexed with polystyrene thin film and heated to 300 <sup>o</sup> C resulting to produce ZnS nanocrystals.

 $Zn(NO_3)_2 \cdot 6H_2O \qquad \begin{array}{c} 1) \text{ NH}_4OH \\ 2) \text{ DDT} \\ \hline EtOH \end{array} \qquad Zn(DDT)_2$ 

DDT = Dodecanethiol

**Scheme 8.** Synthesis of zinc-*bis*(dodecanethiolate).

Nishida and coworkers prepared *gem*-di(iodozincio)methane species.<sup>30</sup> These were prepared from zinc metal and diiodomethane in tetrahydrofuran (THF) with a catalytic amount of PbCl<sub>2</sub> and stirred at ambient temperature for 2 hours (Scheme 9a). Next, 2,2'-bipyridine (bpy) or N,N,N',N'tetramethylethylenediamine (TMEDA) ligands were added and reacted at room temperature for 30 minutes resulting in pale yellow precipitate of the *gem*di(iodozincio)methane species. Due to the Schlenk equilibrium, which is a chemical equilibrium found in Grignard reagents, these materials decomposed to diiodozinc with their respective neutral ligands still attached and could be isolated and characterized via NMR spectroscopy (Scheme 9b). Even though the main focus was to prepare the *gem*-di(iodozincio)methane species, the decomposition product is of interest since a soluble zinc product is obtained which could potentially react with NaSEt to produce soluble zinc thiolate species for SSP materials.



**Scheme 9.** a) Preparation of *gem*-di(iodozincio)methane species. b) General process of Schlenk equilibrium for production of diiodozinc species.

Previous work has been done to synthesize tin thiolate complexes. Barone and coworkers were interested in preparing SnS<sub>2</sub> thin films from a (PhS)<sub>4</sub>Sn precursor (Scheme 10).<sup>32</sup> This complex was produced by simple salt metathesis of tin tetrachloride and sodium thiophenolate.

Scheme 10. Preparation of (PhS)<sub>4</sub>Sn.

# **1.2 EXPERIMENTAL TECHNIQUES**

X-ray diffraction (XRD) is utilized to determine the phase and size of the nanocrystals. An XRD instrument is made of three basic components: an X-ray cathode ray tube, a sample holder, and an X-ray detector. An X-ray source, usually from copper, produces x-rays that will collide with the sample and diffract the x-rays. If the diffracted x-rays are constructive, they will be detected and correspond to lattice parameters of the crystal. This phenomena is described by the Bragg equation  $2d\sin\theta = n\lambda$ . The results can be analyzed via a database to confirm the structure and phase of the sample. In addition, the size of the nanocrystal can be roughly determined using the Scherrer equation,  $\tau = K\lambda/\beta\cos\theta$  where  $\tau =$  mean size of crystal, K = 0.90 which is a dimensionless shape factor that can change depending on actual shape of crystal,  $\lambda = 1.54051$  Å which is X-ray wavelength for Cu alpha,  $\beta =$  line broadening measured by full width at half max in radians, and  $\theta =$  is the Bragg angle, between incident and diffracted beam.

Nuclear magnetic resonance (NMR) spectroscopy is an extremely useful technique for sample characterization. The spin of an atomic nucleus, before application of a magnetic field, is randomly oriented. When a magnet is applied, the nuclear spins orient in a manner that is aligned with (alpha state) or against (beta state) the magnetic field. Only certain atomic nuclei, including <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P, <sup>119</sup>Sn, and <sup>117</sup>Sn, have spins that can be probed by NMR analysis. Electromagnetic radiation from 4 to 900 MHz is applied to the system which will excite the electrons oriented in the alpha state to spin flip to the beta state. The

energy is then released, returning the excited nuclei back down to their original states is called resonance, which produces a fluctuating magnetic field that is detected and converted by Fourier transform into signals at specific frequencies reported in parts per million (ppm) deviation from a reference value. The number of inequivalent nuclei in a structure determines the number of signals produced and will shift depending on the electronic and magnetic environment surrounding nucleus of interest. In addition, each signal can be split into multiple peaks whose number depends on the number of inequivalent nuclei near the nucleus of interest. The intensity of signals can be integrated to provide relative ratios between the inequivalent nuclei. Metals, if they are spin active, can also couple to the nuclei providing even more signals called "satellites." The number of signals, splitting of signals, and integration can be compiled together to provide information about the structure of a molecule.

Inductively coupled plasma optical emission spectroscopy (ICP-OES) is used for determining the elemental composition of a sample. A sample is completely dissolved in a strong acid (usually nitric acid). The sample enters the instrument via peristaltic pump where it is converted to a mist by an analytical nebulizer and exposed to a plasma torch. The plasma torch promotes electrons from the ground to excited electronic states, and when the electrons relax back to the ground state, visible photons are emitted at wavelengths that corresponds specifically to each element. The relative intensities of the wavelengths, relative

to standard calibration solutions, can be used to determine the abundance of each element within the sample.

Solid state ultraviolet visible spectroscopy is utilized to determine the bandgap of a sample. Wavelengths of light varying from 800 to 200 nm are applied to the sample and wavelengths of varying values are absorbed at different efficiencies to excite the ground state electron to an excited state. Lower wavelengths of light are absorbed for larger energy jumps between the two states. Information obtained is a graph of absorbance vs. wavelength. For solids, the *x*-intercept of the high wavelength edge of the absorption profile is measured to determine the minimum band gap using the derived equation eV = 1240  $eV \cdot nm/\lambda$ .

Thermal gravimetric analysis (TGA) is used for solid state decomposition analysis. Two alumina pans, one is the reference and the other is for the sample are placed inside a furnace which are heated to a given temperature. The reference pan accounts for the weight change of the alumina pan upon heating so the weight of the sample is accurately measured. Nitrogen gas is supplied through the furnace to remove any volatile substances upon heating and the weight loss is recorded correlating to the temperature that the loss occurred at providing information about the solid state decomposition.

# **2.0 EXPERIMENTAL**

Starting materials sodium metal (Na), gallium (III) chloride, (GaCl<sub>3</sub>, ultra dry, 99.999%, metal basis), indium (III) chloride, (InCl<sub>3</sub>, anhydrous, 99.99%, metals basis), zinc (II) iodide, (ZnI<sub>2</sub>, 99+%), zinc sulfate heptahydrate, (ZnSO<sub>4</sub> · 7 H<sub>2</sub>O, 99+%), zinc nitrate hexahydrate,  $(Zn(NO_3)_2 \cdot 6 H_2O, 98\%)$ , diethylzinc, ((CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>Zn, 1.0 M in hexanes), tin (IV) tetrachloride, (SnCl<sub>4</sub>, 98%), chloro(triphenylphosphine)gold (I), ( $[(C_6H_5)_3P]AuCI$ , 99+%) ethanethiol, (CH<sub>3</sub>CH<sub>2</sub>SH, 99+%), *t*-butylthiol, (*t*-BuSH, 99+%), ethanedithiol (HSCH<sub>2</sub>CH<sub>2</sub>SH, 99+%), propanedithiol (HSCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SH, 99+%), dodecanethiol (CH<sub>3</sub>(CH<sub>2</sub>)<sub>10</sub>CH<sub>2</sub>SH, 99+%), *p*-toluenethiol, ((CH<sub>3</sub>)C<sub>6</sub>H<sub>4</sub>SH, 99+%), N,N,N',N'tetramethylethylenediamine ((CH<sub>3</sub>)<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>, 99.5%), 1-methylimidizole  $(C_4H_6N_2, 99+\%)$ , diethylsulfide  $(CH_3CH_2)_2S, 98\%)$  were purchased from commercial suppliers. Thiols, 1-methylimidizole, and TMEDA were degassed under vacuum and dried over 4 Å molecular sieves. GaCl<sub>3</sub> was sublimed if it exhibitted appreciable discoloration or was not a crystalline solid. Diethylzinc, Znl<sub>2</sub>, SnCl<sub>4</sub>, GaCl<sub>3</sub>, InCl<sub>3</sub>, NaSEt, NaSPh, and [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]AuCl were used under inert nitrogen atmosphere. All anhydrous solvents were collected from a solvent purification system (SPS). These solvents were further degassed and tested with Na/benzophenone ketyl before use. NMR solvents were dried over molecular sieves and alumina prior use.

All SSPs preparations and manipulations were carried out with oven-dried glassware under inert nitrogen atmosphere using a glovebox or standard Schlenk techniques. NMR spectra were obtained using a Varian JEOL ECX 300

spectrometer. <sup>1</sup>H NMR spectra were referenced using the residual solvent peak of 7.16 for C<sub>6</sub>D<sub>5</sub>H. XRD, solid state UV-Vis, TGA, and ICP-OES data were obtained using Bruker D8 Discover, Shimadzu UV-3101PC, Thermal Analysis SDT Q600, and Varian 715-ES respectively. All instruments were utilized at Idaho State University.

# 2.1 FIRST ATTEMPTS TO PREPARE ZINC THIOLATE MATERIALS

#### Attempted Synthesis of Zinc bis-(tert-butylthiolate)<sup>29</sup> (7)

In a 250 mL round bottom flask,  $Zn(SO_4) \cdot 7H_2O$  (5.727 g, 19.9 mmol), 50 mL deionized water, and 50 mL ethanol were combined. The reaction was stirred for 10 minutes. 25% ammonium hydroxide was added until the precipitated metal hydroxide was fully dissolved. *t*-butylthiol (5.64 mL, 50.0 mmol) was added dropwise and the reaction was stirred for two hours. The resulting white precipitate was collected through vacuum filtration, washed with distilled water and ethanol, and dried under vacuum. A white solid was collected (22.425 g, 463% yield). The literature melting point temperature was 260 ° C while the melting point of the obtained product was 350 ° C. This synthetic route was abandoned in favor of other avenues to produce zinc thiolate complexes.

### Attempted Synthesis of L<sub>2</sub>Zn(SEt)<sub>2</sub> (9) from Znl<sub>2</sub>

In a 20 mL reaction vial, ZnI<sub>2</sub> (32.6 mg, 0.10 mmol) was added to toluene with 1-methylimidizole (16.28  $\mu$ L, 0.20 mmol), and the reaction was stirred overnight. Sodium ethanethiolate (17.18 mg, 0.20 mmol) was added and the

reaction was stirred for 3 hours at ambient temperature. White precipitate was removed by filtration, and the filtrate was evaporated to dryness. The reaction was repeated replacing 1-methylimidizole with tetrahydrofuran (THF) or diethyl sulfide. Only the reaction with diethyl sulfide yielded a white precipitate upon evaporation and was analyzed via <sup>1</sup>H NMR. NMR (C<sub>6</sub>D<sub>6</sub>,  $\Box$ ppm): <sup>1</sup>H NMR; 2.91 (q, 4H, S(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), (t, 4H, S(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), (t, 2H, S(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>).

### Attempted Zinc Thiolate Strategies Using Diethylzinc (10, 11, 12, 13)

In a typical experiment, diethyzinc (500 µL, 1 M in hexanes, 5.26 mmol) was added to 10 mL of toluene. t-butylthiol (1.33 mL, 11.76 mmol) was added dropwise to solution, which was then stirred for 4 hours. The resulting white precipitate was collected via vacuum filtration and dried under vacuum. The resulting percent yield was 49.78% (0.36 g). Letting the reaction proceed longer did not result in higher percent yields. The synthesis was repeated exchanging tbutylthiol for ethanethiol, ethanedithiol, or propanedithiol. All products were insufficiently soluble for <sup>1</sup>H NMR analysis in deuterated acetone, benzene, acetonitrile, DMSO, or chloroform, and were hypothesized adopt polymeric  $(Zn(SR)_2)_x$  structures. These complexes were analyzed by TGA to compare their actual mass loss upon thermolysis to the theoretical value for decomposition of the target  $Zn(SR)_2$  to ZnS.  $Zn(St-Bu)_2$  **10**: Percent yield: 49.78% (0.36 g); TGA residual mass: actual 39.72%, theoretical 39.99%. Zn(SEt)<sub>2</sub> **11**: Percent yield: 36.35% (0.20 g); TGA residual mass: actual: 50.36%; theoretical 51.94%. Zn(κ<sup>2</sup>-SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>S) **12**: Percent yield: 39.62% (0.31 g). TGA residual mass: actual

47.8%, theoretical 56.80% Zn( $\kappa^2$ -SCH<sub>2</sub>CH<sub>2</sub>S) **13**: Percent yield: 30.25% (0.13 g); TGA residual mass: actual 61.67%, theoretical 61.85% .

# 2.2 CURRENT METHODS FOR SYNTHESIZING ZINC THIOLATE MATERIALS Synthesis of Zinc Dodecanethiolate (8)

In a 150 mL round bottom flask, dissolved ZnNO<sub>3</sub> ·  $6H_2O$  (1.223 g, 6.46 mmol) in 42 mL ethanol. Added 25% ammonium hydroxide dropwise until metal hydroxide that formed dissolved. Once dissolved, dodecanethiol (3.27 mL, 12.92 mmol) was added dropwise. The reaction stirred for 2 hours. The resulting white precipitate was collected via vacuum filtration and dried under vacuum resulting in 39% yield (0.75 g) TGA results: actual: 19.89%, theoretical: 20.82%. NMR (C<sub>6</sub>D<sub>6</sub>,  $\Box$ ppm): <sup>1</sup>H NMR; 1.39 (s, 22H, S(CH<sub>2</sub>)<sub>11</sub>CH<sub>3</sub>), 0.97 (t, 3H, S(CH<sub>2</sub>)<sub>11</sub>CH<sub>3</sub>).

## Synthesis of (TMEDA)Zn(SEt)<sub>2</sub> and (IM)<sub>2</sub>Zn(SEt)<sub>2</sub><sup>30</sup> (14,15)

Znl<sub>2</sub> (0.3265 g, 1.00 mmol) and tetramethylethylenediamine (TMEDA) (0.184 mL, 1.23 mmol) were dissolved in 10 mL of ethanol and stirred overnight. The white precipitate was collected by vacuum filtration, washed with hexanes, and dried under vacuum. The product was redissolved product in benzene and added sodium ethanethiolate (2 mol) under inert conditions. The reaction stirred overnight, filtered, pumped down filtrate, and collected a white solid with 57.3% yield (0.26 g). The above experiment was repeated with 1-methylimidizole with 61.08% yield (0.43 g). Characterization results: **TMEDA (14)**: NMR (C<sub>6</sub>D<sub>6</sub>,  $\Box$ ppm): <sup>1</sup>H NMR; 3.09 (q, 4H, SCH<sub>2</sub>CH<sub>3</sub>), 1.96 (s, 12H, NCH<sub>3</sub>), 1.67 (t, 6H,

SCH<sub>2</sub>CH<sub>3</sub>) 1.47 (s, 4H, NCH<sub>2</sub>CH<sub>2</sub>N) 1-methylimidizole (15): NMR (C<sub>6</sub>D<sub>6</sub>, □ppm): <sup>1</sup>H NMR; 7.21 (s, 2H, NCH=N), 7.08 (s, 2H, NCH=CH), 6.13 (s, 2H NCH=CH), 3.09 (q, 4H, SCH<sub>2</sub>CH<sub>3</sub>), 2.48 (s, 6H, NCH<sub>3</sub>), 1.60 (t, 6H, SCH<sub>2</sub>CH<sub>3</sub>).

# 2.3 CURRENT METHODS FOR SYNTHESIZING TIN THIOLATE MATERIALS Synthesis of Sn(SEt)4<sup>32</sup> (16)

In a 100 mL Schlenk flask, tin tetrachloride (0.6022 g, 2.31 mmol) was dissolved in toluene. Sodium ethanethiolate (0.778 g, 9.25 mmol) was added under an inert nitrogen atmosphere and refluxed at 110  $^{\circ}$  C for 2 hours. The white precipitate was filtered off and the filtrate was pumped down resulting in 52% yield (0.600 g). NMR (C<sub>6</sub>D<sub>6</sub>,  $\Box$ ppm): <sup>1</sup>H NMR; 2.76 (q, 8H, SCH<sub>2</sub>CH<sub>3</sub>), 1.21 (t, 12H, SCH<sub>2</sub>CH<sub>3</sub>), <sup>117</sup>Sn and <sup>119</sup>Sn satellites; 2.89 and 2.68 (q, J = 66.6 Hz).

# **2.4 GOLD PRECURSORS AND MATERIALS**

#### Synthesis of NaSEt<sup>33</sup>

In a sealed three-neck round bottom flask, 500 mL of diethyl ether (collected from an N<sub>2</sub>-filled molecular sieve drying column) was added to Na metal (23.0 g, 1.0 mol) inside the glovebox. The flask was brought outside the glovebox and connected to an oven-dried condenser under alternating nitrogen and vacuum atmosphere. EtSH (37.5 mL, 0.5 mol) was added to the flask and produced a cloudy white solution of NaSEt. The reaction was stirred and refluxed for 5 hours. Additional EtSH (37.5 mL, 0.5 mol) was added to the reaction and

stirred overnight under reflux. (On occasions when Na metal remained visible, additional EtSH was added, with additional refluxing, until all metal was consumed.) A white precipitate was formed and remaining volatiles were evaporated under reduced pressure. The white product was dried under vacuum for 1 hour and brought into the glovebox for further use with a 92% yield. NaSEt (21.1 mg, 0.25 mmol) and trimethoxybenzene (42.2 mg, 0.25 mmol) were dissolved in DMSO-D<sub>6</sub> and tested by <sup>1</sup>H NMR for purity based on the integral ratio between methyl signals (1:3). NMR (DMSO, ppm): <sup>1</sup>H NMR; 2.23 (q, 2H, SCH<sub>2</sub>CH<sub>3</sub>), 1.07 (t, 3H, SCH<sub>2</sub>CH<sub>3</sub>).

## Synthesis of Na[Ga(SEt)4] (17)

In the glovebox, sublimed GaCl<sub>3</sub> (1.646 g, 9.35 mmol) was dissolved in benzene in a 100-ml Schlenk flask. Sodium ethanethiolate (3.146 g, 37.40 mmol) was added to the solution and refluxed at 80 <sup>o</sup> C for 2 hours. The resulting solution was evaporated to dryness and recrystallized from benzene layered with pentane to yield **17** as white needles (8.57 g, 68 % yield). NMR (C<sub>6</sub>D<sub>6</sub>, ppm): <sup>1</sup>H NMR; 2.99 (q, 8H, S**CH**<sub>2</sub>CH<sub>3</sub>), 1.49 (t, 12H, SCH<sub>2</sub>**CH**<sub>3</sub>); (CD<sub>2</sub>Cl<sub>2</sub>, ppm): <sup>1</sup>H NMR; 2.73 (q, 8H, S**CH**<sub>2</sub>CH<sub>3</sub>), 1.33 (t, 12H, SCH<sub>2</sub>**CH**<sub>3</sub>).

### Synthesis of (PPh<sub>3</sub>)AuGa(SEt)<sub>4</sub> SSP (18)

Chloro(triphenylphosphine)gold (I) (0.493 g, 1.00 mmol) was dissolved in benzene. Na[Ga(SEt)<sub>4</sub>] (0.336 g, 1.00 mmol) was also dissolved in benzene and added to the gold solution dropwise. The reaction was stirred at ambient temperature overnight. Vacuum filtration was performed and the filtrate was

evaporated to dryness to collect the product as a pale yellow "goo." Pentane was added to the product and allowed to sit for about 1 hour and white, needle-like crystals formed. The crystals were washed and pipetted off with pentane 3 times and dried under vacuum. NMR (C<sub>6</sub>D<sub>6</sub>, ppm): <sup>1</sup>H NMR; 7.49 and 6.98 (m, 6H and 9H, P**Ph**<sub>3</sub>), 3.14 (q, 8H, S**CH**<sub>2</sub>CH<sub>3</sub>), 1.5 (t, 12H, SCH<sub>2</sub>**CH**<sub>3</sub>). <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>, ppm); 5.96.

# Synthesis of Na[Ga(SAr)4] (19)

Na[Ga(SEt)<sub>4</sub>] **(17)** (0.5021 g, 1.49 mmol) was dissolved in 15 mL of benzene in 20 mL reaction vial. P-toluenethiol (0.9246 g, 7.44 mmol) was added to the reaction and stirred overnight. The resulting solution was pumped down, washed with benzene to remove excess thiols, and analyzed via <sup>1</sup>H NMR. NMR (C<sub>6</sub>D<sub>6</sub>, ppm): <sup>1</sup>H NMR; 7.67 and 6.82 (d, 2H and 2H, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>S), 2.01 (s, 3H, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>S).

#### Synthesis of PPh<sub>3</sub>AuGa(SAr)<sub>4</sub> SSP (20)

Chloro(triphenylphosphine)gold (I) (0.5194 g, 1.05 mmol) was dissolved in benzene. Na[Ga(SAr)4] (0.7493, 1.05 mmol) was dissolved in benzene and added to the gold solution dropwise. The reaction was stirred at ambient temperature overnight. The reaction was filtered by vacuum filtration, pumped down filtrate, and produced a white solid in 88% yield (1.062 g). NMR (C<sub>6</sub>D<sub>6</sub>, ppm): <sup>1</sup>H NMR; 7.59 (m, 15H, P**Ph**<sub>3</sub>), 7.48 and 6.85 (d, 8H and 8H, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>S), 2.20 (s, 12H, **CH**<sub>3</sub>C<sub>6</sub>H<sub>4</sub>S). <sup>31</sup>P (C<sub>6</sub>D<sub>6</sub>, ppm) 5.76.

# 2.5 ATTEMPTS TO PREPARE AUIN SSPS

#### Attempted Synthesis of (PPh<sub>3</sub>)Auln(SEt)<sub>4</sub> via Modified Banger Method<sup>39</sup>

In a 50 mL round bottom flask, InCl<sub>3</sub> (24.46 mg, 0.11 mmol) and NaSEt (37.20 mg, 0.44 mmol) was added to methanol and stirred for 30 minutes. PPh<sub>3</sub>AuCl (54.7 mg, 0.11 mmol) was added to the solution and stirred for 24 hours. The resulting solution was filtered, filtrate pumped down, and the white solid was analyzed by <sup>1</sup>H NMR, which indicated the presence of (PPh<sub>3</sub>)AuSEt rather than the intended target. NMR (C<sub>6</sub>D<sub>6</sub>, ppm): <sup>1</sup>H NMR; 7.35 and 6.96 (m, 6H and 9H, P**Ph<sub>3</sub>**), 3.05 (q, 2.5H, S**CH**<sub>2</sub>CH<sub>3</sub>), 1.53 (T, 3.5H, SCH<sub>2</sub>**CH**<sub>3</sub>).

## Attempted Synthesis of (PPh<sub>3</sub>)AuIn(SCH<sub>2</sub>CH<sub>2</sub>S)<sub>2</sub>

In a 100 mL round bottom flask, 1,2-ethanedithiol (87.48 mg, 0.93 mmol) was dissolved in10 mL of methanol, sodium methoxide (0.100 g, 1.85 mmol) was added, and the mixture was stirred for 15 minutes. In a separate vial, InCl<sub>3</sub> (0.103 g, 0.47 mmol) was diluted in 50 mL of methanol and added to the previous solution 1 drop/second. After the addition of InCl<sub>3</sub>, the reaction was stirred for 1 hour. A white precipitate was produced. PPh<sub>3</sub>AuCl (0.2297 g, 0.46 mmol) was added to the solution and stirred overnight. An aliquot of the solution was filtered, and the filtrate was evaporated to dryness to yield a white solid that was analyzed by <sup>1</sup>H NMR. The resulting spectrum was too messy for integration.

# **2.6 THERMOLYSIS STUDIES and Precursors**

## Synthesis of $(Ph_3P)_2Cu(\mu-SEt)_2Ga(SEt)_2^{33}(5)$

In a glovebox, PPh<sub>3</sub> (2.0 mol) was dissolved in 10 mL of THF in a long Schlenk tube. CuCl (1.0 mol) was added to the solution, which was then stirred at room temperature for approximately 4 hours, until the CuCl was completely consumed to yield a cloudy white solution of (Ph<sub>3</sub>P)<sub>2</sub>CuCl. (In some cases, sonication was applied to enhance the solubility of CuCl.) One equivalent of GaCl<sub>3</sub> (1.0 mol) was added and the mixture was stirred in an oil bath at 80 °C for 1 hour, or until the solution was clear. Four equivalents of NaSEt (4.0 mol) was added to the solution and stirred at 80 °C for 24 hours yielding (Ph<sub>3</sub>P)<sub>2</sub>Cu(µ-SEt)<sub>2</sub>Ga(SEt)<sub>2</sub>.To verify completion of the reaction, an aliquot was filtered and the filtrate was evaporated to dryness under vacuum for 20 – 30 minutes and analyzed by <sup>1</sup>H NMR. (Reactions exhibiting less than the expected SEt signals were returned to the oil bath for additional heating.) The entire solution was filtered, and the filtrate was evaporated to dryness yielding colorless crystals. A recrystallization by layering pentane might be needed to produce purer product. NMR (CD<sub>2</sub>Cl<sub>2</sub>, ppm): <sup>1</sup>H NMR; 7.35 (m, 30H, P**Ph<sub>3</sub>**), 2.60 (q, 8H, S**CH**<sub>2</sub>CH<sub>3</sub>), 1.20 (t, 12H, SCH<sub>2</sub>CH<sub>3</sub>); (C<sub>6</sub>D<sub>6</sub>, ppm): <sup>1</sup>H NMR; 7.50 and 7.02 (m, 12H and 18H, PPh<sub>3</sub>), 2.97 (q, 8H, SCH<sub>2</sub>CH<sub>3</sub>), 1.40 (t, 12H, SCH<sub>2</sub>CH<sub>3</sub>).

# Nanocrystal Synthesis using PPh<sub>3</sub>AuGa(SEt)<sub>4</sub> (NC-5/18 a - g)

In a typical reaction,  $(Ph_3P)_2Cu(\mu-SEt)_2Ga(SEt)_2$  **5** (0.2019 g, 0.22 mol) and PPh\_3AuGa(SEt)\_4 **18** (1.7 mg, 2.2 mmol) were dissolved in benzyl acetate. 1,2-ethanedithiol (162.4 mg, 1.72 mol) was added to the resulting solution and stirred at room temperature for 15 minutes. The reaction was heated to 230  $^{\circ}$  C for 1 hour or until solution changed to yellow. Benzyl acetate and excess 1,2-ethanedithiol was removed via centrifugation, washed three times with methanol, and the resulting nanocrystals were dried under vacuum for 1 hour yielding 57 mg. The amount of **18** varied from 0, 1, 6, 8, 10, and 50 mol % for production of nanocrystals **NC-5/18 a- g**.

## Nanocrystal Synthesis using PPh<sub>3</sub>AuGa(SAr)<sub>4</sub> (NC-5/20 a - d)

In a typical reaction,  $(Ph_3P)_2Cu(\mu-SEt)_2Ga(SEt)_2$  **5** (0.0949 g, 0.11 mol) and PPh<sub>3</sub>AuGa(SAr)<sub>4</sub> **20** (2.19 mg, 2.14 mmol) were dissolved in benzyl acetate. 1,2-ethanedithiol (115.7 mg, 1.22 mol) was added to the resulting solution and stirred at room temperature for 15 minutes. The reaction was heated to 230 <sup>o</sup> C for 1 hour or until solution changed to yellow. Benzyl acetate and excess 1,2ethanedithiol was removed via centrifugation, washed three times with methanol, and the resulting nanocrystals were dried under vacuum for 1 hour yielding 27 mg. The amount of **20** varied from 0, 2, 20, and 40 % to produce nanocrystals **NC-5/20 a - d**.

# NANOCRYSTAL CHARACTERIZATION

The resulting nanocrystals **NC-5/18 a - g** and **NC-5/20 a - d** were analyzed via XRD, UV-Vis, and ICP-OES. For XRD, about a 5 mg powder sample was placed on a glass slide and placed on the sample holder. Scans

were collected for 4 hours with a 0.06° step width at a rate of 10 s/step resulting in a 20 scan range from 10 -  $60^{\circ}$ 

Solid state UV-Vis samples were prepared by adding hexane to a 3 mg sample. The sample was pipetted onto a 150 mm Whatman filter paper, and the hexane was allowed to evaporate off. Absorption spectra of the nanoparticles was collected.

ICP-OES data was collected by weighing 20 mg of each nanocrystal and digested in concentrated nitric acid to make a 10 ppm solution. All samples and standards were run within 24 hours.

# **3.0 RESULTS AND DISCUSSION**

# **3.1 PREPARATION AND CHARACTERIZATION OF GOLD PRECURSORS**

First attempts to produce a AuGa SSPs employed reaction conditions similar to those used in the preparation of CuGa SSP **5**.<sup>36</sup> PPh<sub>3</sub>AuCl was added to GaCl<sub>3</sub> and allowed to react at room temperature. After one hour, 4 equivalents of NaSEt were added and the suspension was stirred overnight at 80 <sup>o</sup> C. Instead of producing the desired AuGa SSP, however, this reaction generated metallic gold and unidentified gallium byproducts (Scheme 11).



Scheme 11. First attempts to produce (PPh<sub>3</sub>)AuGa(SEt)<sub>4</sub>.

To avoid this decomposition, we turned to a synthetic route that introduced the thiolate ligands before gold in order to minimize heating of the goldcontaining target. Na[Ga(SEt)4] (**17**) was prepared by treating GaCl<sub>3</sub> with sodium ethanethiolate and refluxing at 80 <sup>o</sup> C for 24 hours. The synthetic intermediate **17** was collected and mixed with PPh<sub>3</sub>AuCl at room temperature (Scheme 12). Filtration and workup yielded a white solid with <sup>1</sup>H NMR shifts and integration ratios matching those expected for (PPh<sub>3</sub>)AuGa(SEt)<sub>4</sub> (**18**) (Figure 9). Further

analysis of **18**'s structure was conducted to better determine the interaction of the gold atom with the thiolate ligands. The metal centers could be linked by two bridging thiolates as in the case of the Cu and Ag analogues, by one bridging thiolate if gold were to adopt its more typical linear geometry, or by none in a tight ion pair of [(PPh<sub>3</sub>)Au][Ga(SEt)<sub>4</sub>]. To distinguish between these possibilities, low temperature <sup>1</sup>H NMR was utilized. At room temperature, only one ethyl signal is observed. If the structure contains bridging and terminal ligands, distinct ethanethiolate environments could decoalesce at lower temperatures if rapid exchange between the two environments occurring at room temperature is sufficiently slowed. (This result is observed in the case of the copper analogue 5.) If only one signal remains at the lower temperatures, such result would be inconclusive and could correspond to either structure; the two ethanethiolate ligands could be exchanging too rapidly even at lower temperatures to be distinguished by <sup>1</sup>H NMR, or might exist as the ion pair in which only one environment exists. To test this hypothesis, **18** was dissolved in CD<sub>2</sub>Cl<sub>2</sub> and analyzed by <sup>1</sup>H NMR at 25 °C, -70 °C, and -95 °C (Figure 10). Even at the lowest temperature of -95 °C, only one ethyl environment was observed. Interestingly, the ethyl environments at the lower temperatures do not even show the relative broadening characteristic of slowed exchange between distinct terminal and bridging ligands. In comparison with (Ph<sub>3</sub>P)<sub>2</sub>Au(µ-SEt)<sub>2</sub>Ga(SEt)<sub>2</sub>(2) and (Ph<sub>3</sub>P)<sub>2</sub>Cu(µ-SEt)<sub>2</sub>Ga(SEt)<sub>2</sub> (5), 18 more resembles 2, which exhibited broadening rather than decoalescence of the ethyl signals. Progressing down group 11 from CuGa SSP (5), to AgGa SSP (2), to AuGa SSP (18), the M-S

interaction appears to become steadily more labile as shown by the NMR exchange rates where Cu-S is exchanging the slowest since two ethyl environments are observed, Ag-S is intermediate with broadening of the ethyl environment, and Au-S is rapid with no relative broadening of the ethyl peaks.



Scheme 12. Synthesis of (PPh<sub>3</sub>)AuGa(SEt)<sub>4</sub> (18).



Figure 9. <sup>1</sup>H NMR spectrum of PPh<sub>3</sub>AuGa(SEt)<sub>4</sub> (18).



Figure 10. Low temperature <sup>1</sup>H NMR spectra of PPh<sub>3</sub>AuGa(SEt)<sub>4</sub> (18).

The stability of 18 was analyzed in both solution and solid phases. In an NMR tube reaction, **18** was dissolved in C<sub>6</sub>D<sub>6</sub> and heated at increasing temperatures.<sup>36</sup> At 80 °C the complex decomposed to metallic gold and uncharacterized gallium byproducts, suggesting an explanation for why initial synthetic attempts at this temperature did not yield the desired product: **18** may have been produced via this methodology, but decomposed at the higher reaction temperature. In solid phase decomposition studies, a sample of the product was slowly heated to 500 <sup>o</sup>C using TGA under nitrogen. As can be seen in Figure 11, the decomposition occurred at about 190 °C as can be seen in the rapid decline in mass. The resulting nanocrystals could be AuGaS<sub>2</sub> or Au + 0.5Ga<sub>2</sub>S<sub>3</sub> indicating gold incorporation within chalcopyrite or production of metallic gold with a gallium sulfide material. The actual decomposition was 39.71 % while the theoretical calculations for AuGaS<sub>2</sub> were 40.70 % and 42.77 % for Au + 0.5Ga<sub>2</sub>S<sub>3</sub>. In addition, metallic gold could visibly be observed in this thermolysis product indicating no incorporation of gold within the chalcopyrite.



TGA of AuGa(SEt)<sub>4</sub>SSP

#### Figure 11. TGA trace of PPh<sub>3</sub>AuGa(SEt)<sub>4</sub> (18)

A more thermally stable precursor, (PPh<sub>3</sub>)AuGa(SAr)<sub>4</sub> (**20**), was also produced in order to better match the decomposition with the CuGa SSP (**5**). AuGa precursor via simple ligand exchange (Scheme 13). In benzene, Na[Ga(SAr)<sub>4</sub>] (**17**) was added to 4 equivalents of p-toluenethiol and allowed to stir at room temperature overnight. A white precipitate Na[Ga(SAr)<sub>4</sub>] (**19**) was collected and washed with benzene for removal of excess ethanethiolates.**19** was added to PPh<sub>3</sub>AuCl to produce (PPh<sub>3</sub>)AuGa(SAr)<sub>4</sub> (**20**), the identity of which was confirmed by <sup>1</sup>H NMR (Figure 12). A solution phase decomposition study of **20** was conducted in the same manner as that of ethyl analog **18**. At 80 °C, there was no visible change in the <sup>1</sup>H NMR spectrum, meaning the product was stable at higher temperatures than (PPh<sub>3</sub>)AuGa(SEt)<sub>4</sub> (**18**). A solid state decomposition study via TGA mirrored these results, with the aryl substituted complex **20** not



decomposing until 260 °C (Figure 13).

**Scheme 13.** Synthesis of (PPh<sub>3</sub>)AuGa(SAr)<sub>4</sub> precursor (**20**) via ligand exchange.



Figure 12. <sup>1</sup>H NMR spectrum of (PPh<sub>3</sub>)AuGa(SAr)<sub>4</sub> (20).



Figure 13. TGA Trace of (PPh<sub>3</sub>)AuGa(SAr)<sub>4</sub> (20).

We also attempted to prepare a Auln SSP, which might behave differently because of the closer match between the sizes of Au and In. A synthesis modified from Banger<sup>39</sup> was utilized in which InCl<sub>3</sub> and NaSEt were dissolved in methanol, and PPh<sub>3</sub>AuCl was added after 30 minutes. When the product was collected from the filtrate and analyzed by <sup>1</sup>H NMR, the spectrum did not show the desired ratio of 15:8:12 for the triphenylphosine hydrogens, quartet ethyl protons, and triplet ethyl protons respectively. Instead, the actual integration were 15:2.5:3.5. Even when the reaction was elevated to 60 °C, the results were the same. These results show that the number of ethanethiolate groups was too low, either because the initial reaction for Na[In(SEt)<sub>4</sub>] was not complete, or because a single thiolate group is being transfered to produce PPh<sub>3</sub>AuSEt (Scheme 14).





and ratios were observed confirming PPh<sub>3</sub>AuSEt was produced.

Scheme 14. Attempted synthesis of a Auln SSP.

In an attempt to prepare a AuIn SSP without access to this apparent decomposition pathway, diluted InCl<sub>3</sub> was added to a mixture of 1,2-ethanedithiol and sodium methoxide in methanol (Scheme 15). (The sodium methoxide served to deprotonate the thiol and produce thiolate *in situ*.). PPh<sub>3</sub>AuCl was then added, and the resulting white solid was collected from the filtrate and analyzed by <sup>1</sup>H NMR. The resulting spectra had low absorbance due to low solubility in benzene and inconsistent environments with peaks only at 7.78 and 7.00 ppm for the phenyl groups in the gold precursor and no proton environments from 1,2-ethanedithiol. These results suggest that the desired AuIn precursor may be too

unstable to be of any use.

Scheme 15. Attempted synthesis of a Auln SSP.

### **3.2 Use of Gold Precursors in Nanocrystal Synthesis**

The goal of this research was to test the limits of the SSP approach by seeing if Au (I) could be incorporated within chalcopyrite materials by thermalizing mixtures of Au and Cu precursor molecules. Solution phase nanocrystal syntheses were conducted in a manner similar to that employed by Adhikari in the preparation of silver-containing materials.<sup>35</sup> Various mixtures containing different ratios of (Ph<sub>3</sub>P)<sub>2</sub>Cu(µ-SEt)<sub>2</sub>Ga(SEt)<sub>2</sub> (5) to PPh<sub>3</sub>AuGa(SEt)<sub>4</sub> (18) or PPh<sub>3</sub>AuGa(SAr)<sub>4</sub> (20) were dissolved in benzyl acetate. 1,2-ethanedithiol was added in excess and the mixture was heated to 180 °C to produce yellow nanocrystals NC-5/18 and NC-5/20 respectively (Scheme 16). The mole percentages of 18 were 0, 1, 6, 8, 10, 20, and 50 % (corresponding to NC-5/18 a - g), and the mole percentages of 20 ranged from 2, 20, and 40 % (NC-5/20 a d) as illustrated in Table 4. These solution phase decomposition studies showed that no matter what percentage of gold source was added, no evidence of Au (I) incorporation was observed within these materials. The XRD depicted characteristic peaks at  $2\theta = 29.1^{\circ}$ ,  $48.7^{\circ}$ , and  $57.2^{\circ}$  correlating to chalcopyrite materials tetragonal CuGaS<sub>2</sub> reference pattern (25-0279 JCPDS-01-082-1513). Incorporation of Au would be expected to change the lattice parameters, and thus shift the values of these signals. In addition, characteristic metallic gold peaks at  $2\theta = 38^{\circ}$  and  $44^{\circ}$  were seen matching the reference pattern for gold (04-0784 JCPDS-01-071-3755) (Figures 14 and 15).



Scheme 16. Nanocrystal synthesis employing varying ratios of 18 and 20 to 5 to produce alloyed nanocrystals NC-5/18 a - g and NC-5/20 a - d.

Mol % CuGa SSP 5	Mol % AuGa SSP Mol % AuGa SSF 18 20		NC
100	0	-	а
99	1	-	b
94	6	-	С
92	8	-	d
90	10	-	е
80	20	-	f
50	50	-	g
100	-	0	а
98	-	2	b
80	-	20	С

60 - 40	d
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Table 4. Solution phase decomposition studies with ratios of 18 or 20 with 5 to

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produce alloyed nanocrystals NC-5/18 a - g and NC-5/20 a - d.
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Figure 14. XRD spectra of nanocrystals NC-5/18 a - g.



Figure 15. XRD spectra of nanocrystals NC-5/20 a - d.

The nanocrystals **NC-5/18 a - g** and **NC-5/20 a - d** were also analyzed via UV-Vis to determine their band gap energies. For bulk CuGaS<sub>2</sub>, the band gap is 2.40 eV.<sup>37</sup> According to the UV-Vis data, the band gaps were characteristic for chalcopyrite material (Figure 16). These ranged from 2.15 - 2.33 eV with no strong correlation to the percentage of the AuGa SSPs **18** or **20** added. The variance in band gaps can be attributed largely to the range in nanoparticle sizes approximated using the Scherrer equation.



Figure 16. Solid state UV-Vis spectra of NC-5/18 a - g and NC-5/20 a - d.

ICP-OES results show the elemental percentages of the materials (Table 5). Each nanocrystal sample was dissolved in concentrated nitric acid. This digestion process does not dissolve elemental gold but should solubilize existing gold (I), and upon addition of nitric acid, gold precipitate could readily be seen. The resulting solution was filtered and the filtrate was diluted and analyzed. Results show the actual percentages of copper and gallium were close to the theoretical predictions. The actual results were slightly lower due to remaining surface thiolate ligands surrounding the nanocrystals, which were not accounted for during the calculation process. In addition, the ratios of Ga:Cu were consistent with the effect of increasing amounts of AuGa SSP introducing additional Ga to the materials.

NC	Band Gap (eV)	Size (nm)	ICP % Ga	ICP % Cu	ICP % Au	Ga/Cu
5/18 a	2.27	2.02	30.8	27.3	0	1.13
5/18 b	2.29	2.21	28.6	25.9	0	1.11
5/18 c	2.33	2.91	23.8	20.9	0	1.14
5/18 d	2.29	2.61	29.5	24.4	0	1.21
5/18 e	2.24	2.02	29.7	23.0	0	1.29
5/18 f	2.10	2.35	21.7	14.09	0	1.54
5/18 g	2.15	2.97	23.5	10.0	0	2.30
5/20 a	2.27	2.02	30.8	27.3	0	1.13
5/20 b	2.19	2.54	24.6	22.7	0	1.08
5/20 c	2.23	2.47	25.7	17.6	0	1.46
5/20 d	2.29	2.87	22.6	11.5	0	1.97

Table 5. Characterization of nanocrystals NC-5/18 a - g and NC-5/20 a - d.

## **3.3 FIRST ATTEMPTS TO PREPARE ZINC THIOLATE COMPLEXES**

As mentioned previously, literature reports describe surprisingly few wellcharacterized zinc thiolate complexes that might serve as starting materials for Zn/Sn or Cu/Zn/Sn SSPs. Ideally, we would like zinc thiolate complexes that are soluble and can readily generate open coordination sites to allow incorporation into larger structures. The methodology reported by Rees was used in attempt to prepare zinc *bis-(tert-*butylthiolate) (7), but the resulting white product had an extremely high yield of 463% and a melting point that deviated by 90 ° C from Rees' reports for the target complex.<sup>29</sup> These results show the intended zinc thiolate was not in fact isolated. The original report offered only ambiguous characterization of the target complex, so different synthetic routes were attempted.

A new route was explored utilizing diethylzinc with various thiols. This acid-base chemistry may yield better results for a few reasons. First, solubility of the reagents is not an issue since both diethylzinc and thiols are soluble in benzene. Second, only methane gas as a byproduct is produced, avoiding the production of halide salts that would need to be filtered off after the reaction, or zincate complexes with associated counter cations. Also, diethylzinc is extremely reactive and has a large thermodynamic driving force to produce zinc thiolates. In an attempt to prepare thiolate complexes, diethylzinc was dissolved in toluene and directly added to excess quantities of various thiols; t-butylthiol, ethanethiol, propanedithiol, and ethanedithiol and were expected to produce zinc thiolates (**10**, **11**, **12**, and **13**) respectively (Scheme 17 and Table 4). White precipitates formed immediately upon reaction, but the precipitates all proved to be insoluble

in benzene, acetone, chloroform, acetonitrile, and dimethylsulfoxide (DMSO). In an attempt to solubilize the presumed zinc thiolates, various ligands were added such as 1-methylimidizole, TMEDA, 1,2-ethanedithiol, diethyl sulfide, and triphenylphosphine. In an attempt to find a system that could solubilize the zinc complex, each zinc product and ligand were mixed in various deuterated solvents (acetone, chloroform, acetonitrile, DMSO, and benzene) and analyzed by <sup>1</sup>H NMR. Regardless of the ligand and solvent set used or additional heating to 80 °C, the white solids 10 - 13 remained insoluble under all reaction conditions, implying that the ligands had failed to bind. The resulting <sup>1</sup>H NMR spectra contained only excess thiol and unbound ligands. One possible explanation for these results is that zinc thiolates adopt a polymeric structure as can be seen in Scheme 18. Table 6 summarizes TGA results for **10** - **13**, comparing the actual residual mass after heating to the theoretical value for the decomposition of a polymeric dithiolatozinc complex to ZnS. The actual and theoretical residual weight values are similar to one another with the actual being slightly lower due to the surface ligands not being taken into account in the calculation. These results are consistent with **10** - **13** containing zinc and thiol groups in 1:2 ratios, and thus provide evidence for a polymeric structure. This structure may be too stable to cleave upon addition of the neutral ligands, therefore preventing formation of a soluble zinc thiolate complex. To prevent the polymeric structure from forming in the first place, experiments were performed in which the neutral ligands were added to diethylzinc first, and followed by addition of the thiol; however, the resulting white solid remained insoluble.



R = t-butyl (10), ethyl (11), propanedithiol (12), ethanedithiol (13)

	R Group				
	<i>t</i> -Butyl (10)	Ethyl (11)	Propanedithiol (12)	Ethanedithiol (13)	
Equivalents	2	2	2	2, 4	
Reaction Time	4 h	8 h	5 h	5 h	
% Yield	49.78	36.35	39.62	30.25	
TGA Theoretical	39.99%	51.94%	56.80%	61.85%	
TGA Actual	39.72%	50.36%	47.80%	61.67%	

Scheme 17. Acid-base route to zinc thiolates.

 Table 6. Summary of polymeric zinc thiolates 10 - 13.



solvent = acetone, chloroform, acetonitrile, DMSO, benzene

Scheme 18. Potential insoluble zinc polymeric structure.

The general strategy reported by Rees and Antolini suggested another possible synthetic route to produce soluble zinc thiolate complexes with neutral ligands to avoid the potential for polymeric formation (Scheme 9).<sup>34</sup> Znl<sub>2</sub> was dissolved in benzene and treated with 2 equivalents of 1-methylimidizole, THF, or diethyl sulfide (all capable of serving as neutral ligands) and sodium ethanethiolate. After the resulting mixtures were filtered and the filtrates were evaporated to dryness, product remained only in the reaction with diethyl sulfide, meaning the 1-methylimidizole and THF reactions must not have produced soluble zinc products. The diethyl sulfide product 9 was further analyzed by <sup>1</sup>H NMR spectroscopy. At room temperature, there were signals at 2.91, 1.44, and 1.27 ppm corresponding to one quartet and two triplet peaks in a 3:1 ratio respectively. While the sample was heated to 70<sup>°</sup> C its NMR spectrum showed a separation of the quartet into two separate quartets, meaning it resulted from protons in two environments with overlapping chemical shifts. The comparison between the two reaction temperatures can be seen in Figure 9. In addition, the sample product was analyzed by TGA and had a 51% mass loss and ICP and contained 21% Zn. From these results alone it is difficult to determine the actual structure of the compound formed and needs to be further analyzed. In a similar reaction, sodium benzenethiolate, with its distinctly different NMR signals in the aromatic region, was used in place of ethanethiolate in an NMR scale version of the above reaction. Results showed characteristic peaks of the ethyl groups in appropriate proton ratios of 2:3, but the absorbance for the benzenethiolate was minimal. Even at elevated temperatures of 80 ° C, there was no change in the
spectra or splitting of the ethyl peaks. These results show that sodium ethanethiolate is needed for the 3:1 ethyl ratio and also the L<sub>2</sub>Zn(SEt)<sub>2</sub> complex was not produced. Again, a new synthetic route was entertained.



Scheme 19. Possible synthetic route to produce soluble zinc thiolate compounds with neutral ligands.



Figure 17. Spectrum of 9 at room temperature and 70  $^{\circ}$  C.

## **3.4 CURRENT METHODS FOR SYNTHESIZING ZINC THIOLATE COMPLEXES**

Another synthetic route explored, based on modification of methods reported by Nishida, was to first introduce neutral ligands to Znl<sub>2</sub>, then treat the product with sodium ethanethiolate. Using the neutral ligands TMEDA and 1methylimidizole in this manner produced zinc thiolate complexes **14** and **15**, both of which are soluble in benzene (Scheme 12). The resulting products were analyzed via <sup>1</sup>H NMR (Figures 18 and 19) and exhibited expected proton ratios for nitrogen ligands bound ethane thiolate ligands. The TMEDA product **14** exhibited ethyl peaks at 3.07 and 1.65 ppm in a 2:3 ratio and 1-methylimidizole product **15** had characteristic ethyl signals at 3.08 and 1.57 ppm. These complexes can potentially be used as precursors for ZnS in their own right, or be used as starting materials for more complex bi- or tri-metallic species. The potential complication with **14** and **15** is it may prove difficult to exchange these strongly bound nitrogen ligands in subsequent synthetic steps.



Scheme 20. Synthesis of soluble zinc thiolate complexes with neutral ligands TMEDA and 1-methylimidizole attached (14, 15).



Figure 18. <sup>1</sup>H NMR spectrum of (TMEDA)Zn(SEt)<sub>2</sub> (14).



Figure 19. <sup>1</sup>H NMR spectrum of (IM)<sub>2</sub>Zn(SEt)<sub>2</sub>(15).

To produce a zinc thiolate without such strongly bound ligands, Antolini's modified method was used to prepare zinc dodecanethiolate 8 (Scheme 13).<sup>34</sup> Unexpectedly, once the zinc dodecanethiolate complex was produced, no further modification to the product was needed to get the product into solution. Simply heating **8** in benzene at 80 <sup>o</sup> C resulted in complete dissolution of the complex without any apparent degradation, and 8 stayed in solution once it was returned back to room temperature. The <sup>1</sup>H NMR spectrum depicts the expected broad peak at 1.39 ppm corresponding to the internal hydrogens, a peak at 3.32 ppm for the CH<sub>2</sub> group adjacent to the sulfur, and a triplet at 0.97 ppm arising from the terminal hydrogens. These peaks exhibit the expected 20:2:3 integration ratio. Unfortunately, this thiolate group is not ideal due to the interference of its broad alkyl NMR signal with other signals of interest. Furthermore, if the thiolate groups of 8 are incorporate into a nanocrystal, the long alkyl groups on the surface would interfere with conductive properties of the material. Nonetheless, this complex complements 14 and 15 as a possible starting point for the preparation

EtOH  $ZnNO_3 6 H_20 + 2 HS(CH_2)_{11}CH_3 \xrightarrow{25 \% NaOH} H_3C(H_2C)_{11}S \longrightarrow C(H_2)_{11}CH_3$ of more complex SSPs.

Scheme 21. Synthesis of soluble zinc dodecanethiolate (8).

## **3.5 CURRENT METHODS FOR SYNTHESIZING TIN THIOLATE COMPLEXES**

We were also interested in producing tin thiolate complexes as a first step for eventual ZnSn SSP. A slight modification of a procedure reported by Barone and coworkers produced a soluble tin (IV) ethanethiolate complex **(16)** that was confirmed via <sup>1</sup>H NMR. Tin has two NMR active isotopes that result in additional splitting of proton signals sufficiently close to the metal nucleus. The binding of thiolate ligands was confirmed by the evidence of <sup>117</sup>Sn and <sup>119</sup>Sn satellites illustrated in Figure 21.

Building from this work, soluble zinc **(8, 14, 15)** and tin thiolate **(16)** precursors might be further combined to produce ZnSn or CuZnSn molecular precursors which could be decomposed to produce CZTS nanomaterials (Figure 20). For example, using previous knowledge of producing these precursors, the zinc and tin thiolate complexes might be reacted together in benzene for production of a ZnSn SSP. Using a molecular precursor approach, the ZnSn SSP could be reacted with Cu SSP and decomposed to produce CZTS. Currently, work to produce these ZnSn SSP materials continues.



Figure 20. Potential strategies for CZTS nanomaterials via the SSP approach.



Figure 21. <sup>1</sup>H NMR spectrum of Sn(SEt)<sub>4</sub> (16).

## 4.0 CONCLUSION

The SSP approach offers the potential for kinetic control over the composition of materials. This consideration becomes increasingly important as these materials become more complex. Previous work has demonstrated incorporating Ag within chalcopyrite materials, so we sought to test the limits of the SSP approach and incorporate Au. As explained previously, gold (I) is difficult to incorporate within chalcopyrite materials due to its susceptibility towards reduction and geometric preferences different than those of Cu and Ga. One approach for gold (I) incorporation into these materials is utilizing the SSP approach which from previous results had the ability to incorporate Ag into the chalcopyrite phase it naturally doesn't adopt. However, according to our results thus far, it doesn't appear to have any gold (I) incorporation within the chalcopyrite structure. In our first approaches, we analyzed nanocrystals formed by the solution phase decomposition of **5** and **18** for production of nanocrystals NC-5/18 a-g. One possible explanation for the lack of incorporation is that 18 decomposes at much lower temperatures than 5, perhaps before it has the chance to interact with a nascent chalcopyrite structure formed by 5. To remedy this problem, the ethanethiolate ligands were exchanged with p-toluenethiolate ligands to create the aryl AuGa SSP analogue **20**, with an increased decomposition temperature more closely matching that of 5. However, gold was still not incorporated within the chalcopyrite materials produced with **20**. Another avenue that is currently being explored is exchanging the 5 ethanethiolate ligands for benzylthiolate ligands. This change should reduce the decomposition

69

temperature, allowing nanocrystal synthesis to be performed under conditions where thermodynamic considerations are less likely to dominate. The research done thus far exhibits the limits of the SSP approach.

The limits of the SSP approach were also tested in the first steps toward their application to the case of CZTS. First, we sought to synthesize soluble zinc and tin precursors for future production of CZTS precursors and materials. It was found that solubilizing zinc thiolate precursors is extremely difficult, and likely requires incorporation of large bulky thiolate ligands (dodecanethiolate) or incorporation of neutral ligands (TMEDA or 1-methylimidizole). Products with neutral ligands **14** and **15** pose problems due to difficulty in removal of these ligands, while zinc dodecanethiolate **8**, even though soluble, may ultimately pose problems of its own due to its long alkyl chain. In addition, a soluble tin thiolate complex was synthesized and characterized. Currently, efforts are underway to mix the soluble tin and zinc complexes together to prepare a SnZn SSP.

In conclusion, two AuGa SSPs (**18** and **20**) have been produced and we have been able to modify the thiolate ligands to adjust the decomposition temperature of the compounds. Regardless of these modifications, gold has not been incorporated within the chalcopyrite material exhibiting the limit to the SSP approach, and there is no guarantee that this approach will overcome the thermodynamic considerations for production of target materials. These results highlight the large discrepancy between the behaviors of Au and Ag. Synthesizing zinc thiolate materials as a first step for production of a SSP has proven to be difficult due to solubility issues or undesirable ligands on the

70

complex. However, first steps for ZnSn SSP production are underway.

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