

# **CHAPTER 1.**

## **Introduction.**

## 1.1. Introduction

New materials have a profound effect on communications, the price of energy for our homes and vehicles and the preservation of our environment. All these aspects of our life and more are impacted by the development of materials with either revolutionary properties or by the refinement of known materials that allows for the cost effective processing and distribution of new products.<sup>1</sup> Fundamental scientific investigation, especially in solid-state sciences, has in the past provided the foundation for technological progress and economic growth.<sup>2</sup> While the cornerstone of solid-state chemistry has been the cataloging of crystalline structures, an understanding of structure property relationships rests on the dynamic processes of solids.<sup>3</sup> For example, the stability of crystalline polymorphs with regard to one another can be critical to a materials performance. A dynamic view of solids also lends itself to the development of "smart materials" that can be used in devices with sensing, processing and actuating functions to respond their environment.<sup>4</sup> The field of heterogeneous catalysis is another area rich with examples of solids chemically modified by design and where consideration of not only bulk properties, but reactivity at the interface of the solid with gas and liquid phases becomes critical to meeting performance goals.<sup>5</sup> As solid-state chemistry moves toward the rational synthesis of designed materials, understanding reaction mechanisms becomes increasingly important in gaining synthetic control over composition and morphology. The research reported in this thesis emphasizes the dynamic interplay between structure and properties that is the fundamental science on which technical advances can be built.

The interdependence of dynamic properties and structure in the areas of polymorphism, photoluminescence and gas-solid reactivity for some ternary cuprous metal halides are reported in this thesis. The structural chemistry of this class of materials displays features such as close-packed anion sublattices with different filling patterns by interstitial cations, which raise fundamental structural questions. A mechanism for conversion of a metastable  $\text{CuAlCl}_4$  phase to the thermodynamically stable phase is proposed and supported with kinetic studies. Structural considerations will be shown to be important in understanding the brilliant blue photoluminescence of  $\text{CuAlCl}_4$ . The reversible binding of small molecule olefins and aromatics, as well as carbon monoxide and nitric oxide, to solid  $\text{CuAlCl}_4$  is accompanied by dramatic and reversible structural changes. These structural changes are in turn related to the separations and catalytic potential of solid ternary cuprous metal halides.<sup>6</sup> Indeed, in the solution phase  $\text{CuAlCl}_4$  is used to purge effluent gases of CO in the industrially important COSORB process<sup>7</sup> and the use of toluene solutions of  $\text{CuAlCl}_4$  in separations of olefins from paraffin fractions and from each other has been reported in the patent literature.<sup>8</sup> The  $\text{CuCl}/\text{AlCl}_3$  system is used in the homogeneous catalysis of: a) the preparation of polyphenylene conductive polymers,<sup>9</sup> b) the preparation of extended, all benzenoid hydrocarbons,<sup>10</sup> c) the formylation of aromatic compounds (Gatterman-Koch reaction) d) synthesis of carbonic acid dialkyl, alkyl aryl or cycloalkyl esters from CO and the appropriate alcohol,<sup>11</sup> e) and as a co-catalyst with  $\text{Al}(\text{C}_2\text{H}_5)_n\text{Cl}_{3-n}$  ( $n = 1, 2$ ) in the oligermization of olefins.<sup>12</sup> By way of introduction to the structure and reactivity of the solid cuprous metal halides it is useful to consider (a) the oxide-halide analogy which motivated the initial study of this system, (b) the chemical background of copper(I) which

makes it of interest as a component for our materials, (c) periodic trends which are expected to influence the chemistry of this system.

## **1.2. Oxides to Halides, A Charge Matching Strategy**

Metal halides are important as catalysts, ionic conductors and also display useful optical properties.<sup>13</sup> Microporous oxide materials such as zeolites and clays are important in separations and catalysis and offer promise as matrices for arrays of nanoscale optical and electronic materials.<sup>14</sup> One thrust of the Martin group research program is to wed the reactivity of halides with the size and shape selectivity of microporous materials.<sup>15</sup> Zeolites are three dimensional frameworks of corner sharing tetrahedral metal oxide building blocks, which form channels and cages large enough to be occupied by guest molecules. Clays are lamellar materials, built up of metal oxide tetrahedral and octahedral building blocks, which possess the ability to intercalate small molecules between the metal oxide sheets. One source of synthetic targets is to mimic well known structural crystal chemistry of these two and three dimensional oxide networks with new metal halide analogs.

The preparation of metal halide analogs of metal oxides recognizes that by replacing oxides (or other chalcogenides) with halides the charge of the anion sublattice is halved. Metal halide cations with half the charge of the metal oxide cations, and a propensity for the same coordination geometry, are chosen to form the isotopic composition. For example, in silicates, the principle tetrahedral building block is  $\text{SiO}_4/2$ . The Si cation has an oxidation number of 4+ balanced by two oxide anions, each with

oxidation numbers of 2-. By replacing oxides with chlorides the charge on the anion sublattice is halved and by selecting zinc as the cation (with an oxidation number of 2+ and known preference for tetrahedral coordination), ZnCl<sub>2</sub> phases built up of corner sharing tetrahedra are formed that share known topologies with the silicates.<sup>16</sup> This kind of charge matching strategy can be extended to the important class of aluminophosphates, materials that are themselves related to silicates by the substitution of charge matched cations.<sup>17</sup> Consider that if half the silicon's in SiO<sub>2</sub> are replaced with aluminum and half with phosphorous to formulate AlPO<sub>4</sub>, then the sum of the paired cation oxidation numbers in both stoichiometries ( 2 SiO<sub>2</sub> vs. AlPO<sub>4</sub> ) is the same. Both aluminum and phosphorous are tetrahedrally coordinated in aluminophosphates and provide the framework for a variety of templated structures.<sup>18</sup> One can extend this strategy to metal halides by utilization of cations one column to the left and one to the right of the parent cation. For example, going to the left and right of Zn<sup>2+</sup> in the periodic table one may select Cu<sup>+</sup> and Al<sup>3+</sup> cations, both of which favor tetrahedral coordination. Thus CuAlCl<sub>4</sub> can be considered a halide analog to AlPO<sub>4</sub> and as such may provide a framework for constructing templated microporous metal halides. As will be demonstrated below, however, even in the absence of a templated microporous framework, the condensed phases of CuAlCl<sub>4</sub> exhibit remarkable reconstructive framework flexibility in their ability to reversibly sorb small molecules such as CO, olefins, and aromatics.

While the charge matching strategy emphasizes the structural analogies between oxides and halides it is also informative to consider some of the structural differences. For example, in silicates the Si-O-Si bond angle is typically in the range from 140°-150°, whereas in zinc chlorides the Zn-Cl-Zn bond angle is closed down to 109.6°. In the case

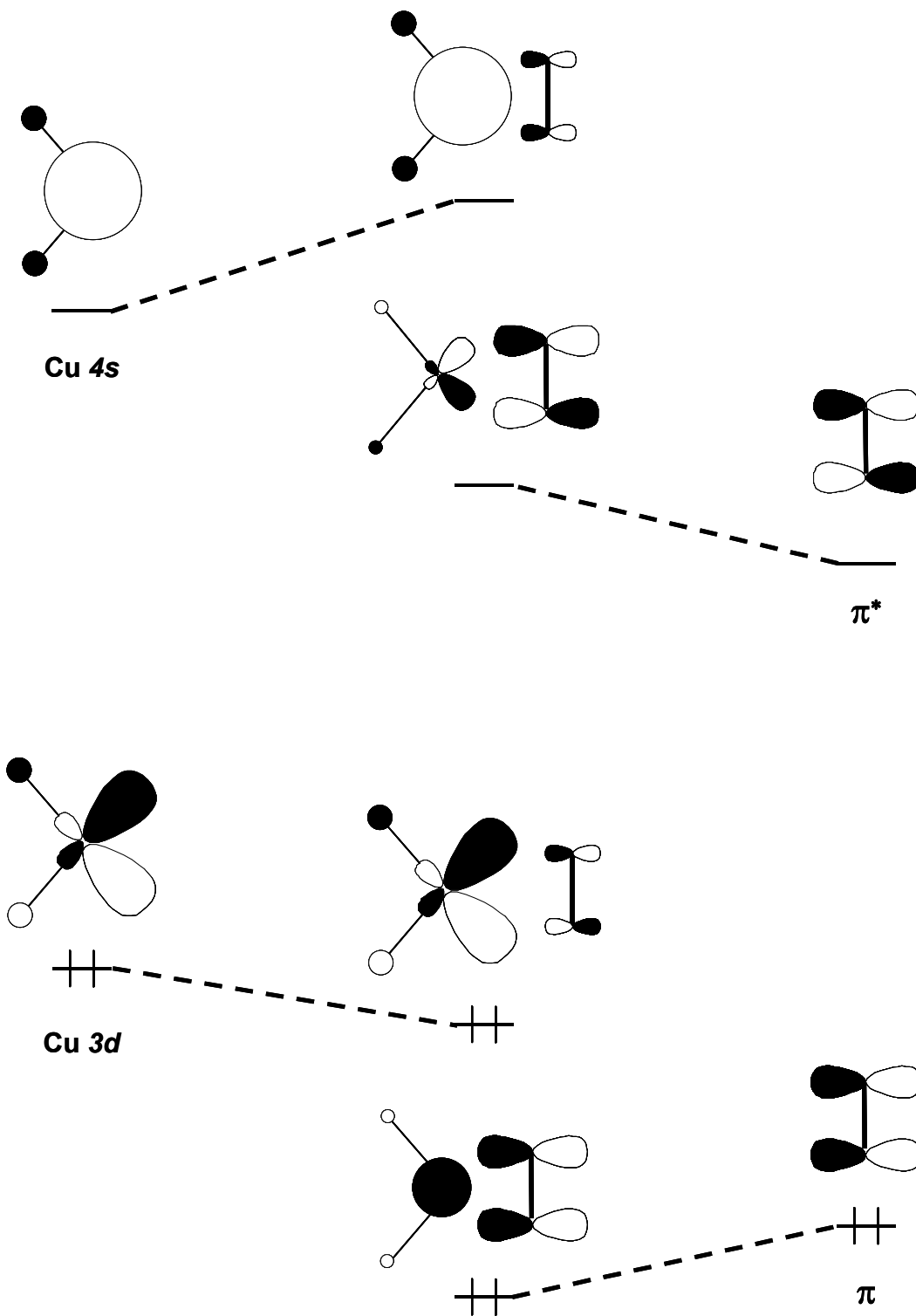
of silicon a larger M-X-M bond angle is required to minimize cation-cation repulsion.<sup>19</sup> The longer metal chloride bond length and lower cation charge reduces cation-cation repulsion in zinc chlorides, thus the smaller M-X-M bond angle is observed. As a consequence of the tetrahedral bond angle at both the metal and the anion, the ZnCl<sub>2</sub> network can be described as a close-packed anion sublattice in which one quarter of the tetrahedral interstices are filled with cations. Zinc chloride adopts both cubic close-packed (*ccp*)<sup>16</sup> and hexagonal close-packed (*hcp*)<sup>20</sup> anion sublattices, structures seen again and again in metal halide chemistry as well as more generally in descriptive crystal chemistry.<sup>21</sup> The pervasiveness of such archetypal structures underlies the utility of the charge matching approach to selecting synthetic targets.

### 1.3. The Chemistry of Copper (I)

One incentive offered by copper in the design of new materials is that it is widely available and relatively inexpensive. The versatile reactivity of copper(I), as demonstrated by the rich solution phase chemistry of catalysis and separations, makes this oxidation state potentially useful in designing new materials. The range of copper(I) reactivity can be classified in three broad categories; 1) Lewis acid/base reactions, 2) oxidation reduction electron transfer reactions, and 3) photochemical reactions. This breadth of reactivity rests on the ability of copper(I) to act as both a  $\sigma$  electron acceptor and a  $\pi$  electron donor. The frontier molecular orbital diagram in Figure 1.1 illustrates the dual acceptor/donor role of copper(I) with an olefin. The high lying filled orbital in Figure 1.1 is a metal-ligand anti-bonding  $\sigma^*$ , which is strongly copper 3*d* in character,

and acts as an electron donor to the low lying empty  $\pi^*$  orbital on the olefin. The low lying empty orbital that is largely copper 4s in character accepts electron density from the high lying filled  $\pi$  orbital on the olefin. This combination of  $\sigma$  Lewis acidity and  $\pi$  Lewis basicity is the foundation for the use of Cu(I) in olefin separations.<sup>8</sup> The interaction of the bound  $\pi$  systems and Cu(I) can lead to electron transfer when the redox potentials are favorable.<sup>22</sup> Likewise, in the photochemistry of cuprous aromatic and olefin complexes, both the conformations favored by copper(I)'s dual  $\sigma$ -acid/ $\pi$ -base character and the energetic proximity of the frontier orbitals facilitates skeletal rearrangements and photocycloaddition reactions.<sup>23</sup>

The first reports that Cu(I) will bind  $\sigma$ -donor /  $\pi$ -acceptors such as ethylene were made a hundred years ago.<sup>24,25</sup> As might be expected, isoelectronic compounds of Ag(I) and Hg(II) were also discovered to bind olefins and aromatics.<sup>26,27</sup> This chemistry was applied to olefin and aromatic separations by the petrochemical industry in the first half of the twentieth century.<sup>28,29,30</sup> Early efforts to explain the structure and bonding of copper(I) olefin complexes utilized resonance structures, which delocalized the electrons between the carbon-carbon double bond and the metal.<sup>31</sup> Fifty years ago a more satisfactory molecular orbital model emerged, the Dewar-Chatt-Duncanson model, named in honor of its early proponents.<sup>32</sup> The Dewar-Chatt-Duncanson model of transition metals bound to unsaturated organic compounds first described the  $\sigma$ -donation from the olefin to the transition metal and  $\pi$ -back-bonding of electron donation from the metal to the olefin. Developments in the patent literature seemed to move in two



**Figure 1.1.** Molecular orbital diagram showing the binding of a  $\text{Cu(I)L}_2^+$  fragment with an olefin. This schematic illustrates  $\text{Cu(I)}$ 's role as a  $\pi$ -donor and a  $\sigma$ -acceptor.



general directions in terms of applying the copper(I) Lewis acid/base chemistry to separations technology. One direction built on the original reports of sorption by CuCl/HCl solutions sought to increase the efficiency by going to the CuBF<sub>4</sub>/HF systems for separations of olefin/paraffin mixtures.<sup>33</sup> The second direction made use of competitive binding between olefins and aromatics to copper(I).<sup>8</sup> In this latter work benzene or toluene solutions of ternary cuprous halides, M<sup>I</sup>M<sup>III</sup>X<sub>4</sub> (M<sup>I</sup> = Cu, Ag) (M<sup>III</sup> = B, Al, Ga, In, Tl) (X = F, Cl, Br, I) are cited with CuAlCl<sub>4</sub> apparently being preferred. As recently as the 1970's technology based on the ability of CuAlCl<sub>4</sub> in toluene solution to purge gaseous effluents of carbon monoxide was marketed to the petrochemical industry as the COSORB process, which remains in use today.<sup>34, 35</sup> Both mono- and diolefin, as well as mono- and di-aromatic and mixed olefin aromatic complexes of ternary cuprous metal halides are reported in the patent literature.<sup>36</sup> These complexes are reported as solution species, and as isolated materials in either solid or liquid phase at ambient temperatures. The mono- and diolefin cuprous metal halide complexes have not been well characterized structurally. Of the mono- and di-aromatic cuprous metal halide complexes, only two crystal structures, those for mono-benzene adducts of CuAlCl<sub>4</sub> and AgAlCl<sub>4</sub>, were known prior to the present investigation. The future development of the Lewis acid/base adduct formation using ternary cuprous metal halide salts may lie with the development of "facilitated transport membranes" to replace the cryogenic separation of ethylene and other olefins.<sup>37</sup> Current technology relies on Ag(I) exchanged membranes and is still in its infancy.<sup>38,39</sup>

The ability of cuprous halides to bind with olefins has been exploited in another manner in traditional organocuprate chemistry, which is important both for laboratory

and industrial syntheses.<sup>40</sup> The simplest fundamental organocuprate unit is a linear  $[\text{CuR}_2]^-$  anionic fragment, where R is an organic moiety (e.g. alkyl, aryl, etc.). One R group is transferred from linear cuprate, most often to an unsaturated organic molecule.<sup>41</sup> The  $[\text{CuR}_2]^-$  anion belongs to a family of linear cuprous anions in which the HOMO is the ligand metal anti-bonding combination which utilizes the copper  $3d_{z^2}$  orbital and the LUMO are the degenerate non-bonding copper  $4p$  orbitals that are orthogonal to the axis of the molecule. The low lying empty  $4p$  orbitals are both energetically and sterically predisposed to act as  $\sigma$ -acceptors and the high lying unsaturated organic  $\pi$  orbitals as  $\sigma$ -donors. The copper  $3d_{xz}$  or  $3d_{yz}$  orbitals are also disposed to act as  $\pi$ -donors to the low lying empty  $\pi^*$  of the unsaturated bond. One can visualize how bending the R-Cu-R bond will enhance the  $\pi$ -donor character of the copper(I) and computations suggest that when the R-Cu-R bond angle is bent to  $\sim 150^\circ$  the orbital diagram given in figure 1.1 is a good description of its frontier orbitals.<sup>42</sup> While most mechanistic descriptions of organocuprate addition reactions to unsaturated substrates invoke the formation of a  $\pi$ -complex as described above, the following steps vary according to the unsaturated system and specific organocuprate used. Commonly the organocuprate is prepared by transmetallation of an alkyl lithium compound using a cuprous halide and the resulting solution species is an aggregate of organocuprate and lithium halide units. The exact nature of these aggregate species has been the subject of much study and debate.<sup>41,42,43</sup> Following the formation of the  $\pi$ -complex in the important  $\alpha,\beta$ -enone addition, two possibilities are generally considered for the transport reaction 1) an organocuprate intermediate in which the formal oxidation state is copper(III) intermediate is formed, 2)

a carbocupration intermediate in which the  $\text{RCu-R}$  adds across the double bond and the copper(I) formal oxidation state remains unchanged. The existence of the copper(III) intermediate is supported by the existence of compounds where the crystal structure shows square planar coordination of a formally  $d^8$  copper and by computational studies.<sup>42</sup> Copper(III) organocuprate intermediates are also invoked in the transfer reactions with alkylhalides. This latter hypothesis has largely supplanted earlier models in which the two copper(I) of an organocuprate dimer are oxidized to copper(II).

While the  $\text{Cu(II)/Cu(I)}$  redox couple is not generally seen as playing a role in organocuprate transfer reagent chemistry it is of overriding importance in other areas. One unambiguous example of  $\text{Cu(II)/Cu(I)}$  redox chemistry is the use of cuprous halides in atom transfer radical addition.<sup>22</sup> The copper(I) complex is oxidized to copper(II) upon reduction and abstraction of a halogen atom from an alkyl halide, which leaves an alkyl radical free to undergo an addition reaction to an olefin. Subsequent reduction of the copper(II) accompanies the halogenation of the resultant radical intermediate. This reaction has been further adapted to act as part of a “living” polymerization process (Atom Transfer Radical Polymerization) in which the polymerization is controlled by the reversible, metal-catalyzed, generation of propagating radicals.<sup>44</sup> Changing the  $\sigma$ -donor and  $\pi$ -acceptor character of the ligands in the copper(I) complex effects the equilibrium constant for the abstraction and thus the overall rate, which is dependent on the concentrations of copper(I) activator and copper(II) deactivator. Good  $\pi$ -acceptors, such as aromatic amines, slow the reaction rate by stabilizing the copper(I) oxidation state (i.e. raising the oxidation potential), compared with aliphatic amine ligands. Thus by changing the ligand coordination sphere of the copper it is possible to tune the

Cu(I)/Cu(II) redox potential. Similarly, in the bioinorganic chemistry of copper, model compounds frequently use histidine and cytosine analogs as ligands to tune the redox potential of the copper half reaction.<sup>45</sup> Biologically important copper containing proteins include “blue” copper proteins<sup>46</sup> and other oxidases,<sup>47</sup> nitrogen oxide reductases,<sup>48</sup> and hemocyanins which reversibly bind dioxygen.<sup>49</sup> It is interesting to speculate on similar redox chemistry occurring in heterogeneous catalysis. For example the oxidation of carbon monoxide utilizes mixed metal oxides in which copper may play a similar role to the role of copper in the oxidase enzymes.<sup>50</sup> Another parallel between heterogeneous catalysis and bioinorganic catalysis is the reduction of nitrogen oxides by copper impregnated ZSM-5.<sup>51</sup> Model studies of the active sites in enzymes focus not only on the composition, but also the geometry of the first coordination sphere. It is well known that chelating ligands which force a square planar geometry on four coordinate Cu(I) compounds favor the cupric oxidation state while a more tetrahedral arrangement of ligands favors the cuprous oxidation state.

The effect of tetrahedral versus square planar coordination geometry on redox potential is explained by considering the relationship between the high lying filled orbitals of the two geometries, which are metal  $d$  in character. In the tetrahedral geometry the  $d$  orbitals are grouped as the metal ligand anti-bonding, triply degenerate,  $t_2$  set of orbitals and the basically non-bonding, doubly degenerate  $e$  set. In a gedanken experiment, one may compress the tetrahedron along one of the two fold symmetry axes to flatten it into the  $D_{4h}$  square planar geometry. The orbital interaction effect of this compression on the  $d$  orbitals is to take one of the  $t_2$  orbitals and raise it in energy by increasing its anti-bonding character ( $b_{1g}$  in  $D_{4h}$ ) and lowering the energy of the

remaining two orbitals of the triply degenerate set to the non-bonding ( $e_g$  orbitals in  $D_{4h}$ ). There is a descent in symmetry of  $e$  orbitals of the  $T_d$  point group, which transform in  $D_{4h}$  as the  $b_{2g}$ , which remains non-bonding, and  $a_{1g}$ , which becomes anti-bonding in character as the tetrahedron is compressed and raised in energy. The relationship between the  $T_d$  and  $D_{4h}$  geometries can be viewed as a first order Jahn-Teller distortion upon a single electron oxidation of copper(I), i.e. upon going from  $d^{10}$  to  $d^9$ . It should be noted that the  $D_{4h}$  can also be related to  $O_h$  by first order Jahn-Teller distortion and in fact many square planar cupric compounds show long axial interactions. An interesting example in light of the later discussions of  $CuAlCl_4$  is the molecular species  $Cu(AlCl_4)_2$ . The copper(II) is coordinated by the edges of two  $[AlCl_4]^-$  tetrahedra in a slightly distorted square planar fashion with short equatorial Cu-Cl bonds of 2.30(1) Å and 2.29(1) Å, but there are also long axial Cu-Cl contacts of 2.96(1) Å to terminal chlorides of molecular units above and below the  $[CuCl_4]^{2-}$  plane.<sup>52</sup>

The photochemistry of copper(I) complexes does not have the same economic importance as the Lewis acid/base however it is of practical and theoretical interest in the skeletal rearrangement of alkenes, as well as in a variety of other photo-induced and photo-assisted reaction.<sup>53</sup> The optical properties of copper (I) are dominated by its closed shell  $3d^{10}$  electron configuration. Unlike other often highly colored transition metal halides (e.g.  $3d^9 Cu^{2+}$ ) there are no d-d transitions and the inter-orbital  $3d-4s$  energy gap lies in the blue to ultraviolet region of the spectrum, yielding typically yellow or colorless compounds, in the absence of ligand centered transitions or charge transfer bands.<sup>54</sup> One of the simplest photochemical processes is the absorption and subsequent emission of light. A diverse range of materials, in which copper(I) serves as the

luminescent activator, exhibit emissions across the visible spectrum. Copper(I) doped zinc chalcogenide phosphors are used commercially in color TV's and computer monitors. Because it often emits in the blue region, copper(I) containing materials are candidates for blue lasers sought after as components in short wavelength optical information storage systems. When bound in a Lewis acid/base complex with unsaturated organic molecules copper(I) plays an important role in photo-assisted rearrangements and addition reactions. An interesting example is a scheme, which seeks to utilize the photo-assisted rearrangement of copper(I) norboradiene complexes to form the strained quadricyclene as a solar energy storage system.<sup>55</sup> The utility of the copper(I) in this photo-assisted process is to move the absorption from the ultraviolet region of the spectrum into a lower energy spectral region more practical for solar energy applications. The coordination of the Cu(I) makes available filled copper 3d orbitals within the HOMO-LUMO gap of the norboradiene, providing a low energy metal to ligand charge transfer band to access a photo-excited intermediate on the pathway to quadricyclene. In another well-studied reaction, norbornene can undergo a photocycloaddition catalyzed by Cu(I). Both LMCT (copper 3d to olefin  $\pi^*$ ) and MLCT (olefin  $\pi$  to copper 4s or 4p) charge transfer bands are observed in the UV-visible spectrum of the Cu(I)-norbornene complex. Photo-excitation into the former creates a cationic olefin free radical, and photo-excitation into the latter creates an anionic olefin free radical. Either one of these two ionic, free radical, excited states offers a stepwise route to the formation of the photocycloaddition product, as well as a third possible pathway, the orbital-symmetry controlled synchronous route. The actual mechanisms for these photocycloaddition

reactions is not unambiguously known at this time and may vary depending on the olefins involved.

Despite the versatile utility of copper(I) cited above, its practical use has often been limited by its sensitivity to moisture. On a planet whose surface is three quarters water blanketed by an oxygen rich atmosphere, the aqueous standard half potentials of the reduction to copper metal are important. These are 0.52 V and 0.34 V respectively for Cu(I) and Cu(II) and 0.15 V for the reduction of Cu(II) to Cu(I).<sup>56</sup> The disproportionation reaction,  $2\text{Cu}^+ = \text{Cu}^0 + \text{Cu}^{2+}$ , which has a standard cell potential of 0.37 V, is thermodynamically favored at standard concentrations, thus rendering most Cu(I) compounds very moisture sensitive. Very often a material is prepared using the more stable Cu(II) oxidation state and reduction to Cu(I) occurs *in-situ*. In the case of copper doped zinc chalcogenide phosphors this sensitivity is overcome by coprecipitation of cupric salts with the zinc sulfide. Sintering at high temperature dopes the sublattice with the luminescent Cu(I) defects, the Cu(II) having been reduced by the formation of volatile elemental sulfur.<sup>57</sup> In some cases the disproportionation may be a desired reaction, hence the investigation of volatile cuprous coordination compounds as precursors for the MOCVD of thin copper films as circuit components for the microelectronics industry.<sup>58</sup>

The oxidation-reduction potentials of the Cu(II)/Cu(I) couple can be tuned by manipulation of the coordination environment of the metal. It is well known that a first order Jahn-Teller distortion of a hypothetical octahedral  $d^9$  Cu(II) yields the square planar coordination typical of Cu(II) compounds. Much of the bioinorganic chemistry of copper involves trying to tune the Cu(II)/Cu(I) redox couple by a judicious selection of

chelating histidine and cysteine analogs which favor either the tetrahedral or square planar geometry.<sup>59</sup> The oxidation of Cu(I) to Cu(II) favors the square planar geometry, over the tetrahedral because the energy cost of raising a singly occupied Cu  $3d$  centered metal-ligand  $\sigma^*$  orbital, in contrast to a doubly occupied orbital, is paid for by lowering the energy of another doubly occupied Cu  $3d$  centered metal-ligand  $\sigma^*$  orbital. The first coordination sphere of copper(I) is not limited to tetrahedral, but exhibits a rich diversity of geometries including three coordinate trigonal planar, two coordinate linear and a whole range of intermediate geometries whose stability can be explained by the symmetry allowed mixing of the filled Cu  $3d$  with the empty Cu  $4s$  and Cu  $4p$  orbitals (second order Jahn-Teller distortion).<sup>60</sup> These basic units can act as building blocks for solids, packed as 0-dimensional molecular species, 1-dimensional chains, double chains, helices and so on, 2-dimensional layered compounds, and 3-dimensional extended frameworks. Of particular note are the distorted edge sharing tetrahedra of  $\text{CuLX}_3$ , which are assembled in cubane fashion in the family of  $\text{Cu}_4\text{I}_4\text{L}_4$  ( $\text{L} = \text{alkylamine}$ ).<sup>61</sup> The connectivity of the higher dimensional solids is usually between corner or edge shared polyhedra, often distorted tetrahedra with a stable electron configuration of two largely anti-bonding  $d$  orbitals over three largely non-bonding  $d$  orbitals.<sup>62</sup>

To conclude this brief overview of copper(I) reactivity, it is seen that copper(I) is well represented in three major categories of reactions, 1) Lewis acid/base, 2) oxidation/reduction and 3) photochemical. Studies that help understand the structure reactivity relationships of copper(I) compounds are of basic scientific interest across a number of disciplines and may have substantial economic impact as well.



## 1.4 Scope

This work will examine the static structures and physical properties of cuprous tetrachloroaluminate and related compounds, then moves to a more dynamic structural description of polymorphism and reactivity of these materials. The brilliant blue luminescence of  $\text{CuAlCl}_4$  is presented in Chapter 2, where it is shown to arise from a convergence of crystallographic isolation of the copper centers and a fortuitous degree of spin orbit coupling which favors radiative relaxation from a formally spin-forbidden, triplet excited state. In Chapter 3,  $^{63}\text{Cu}$  solid state MAS NMR is used to probe the kinetics of the  $\beta$ - to  $\alpha$ - $\text{CuAlCl}_4$  first order phase transition and a mechanism is proposed which relates the two structures by atomic displacements of the tetrachloroaluminate anions and cuprous cations. The Chapter 4 continues the theme of dynamic processes in solids with a report on the reversible sorption of ethylene by  $\alpha$ - $\text{CuAlCl}_4$ , including structural and mechanistic considerations.

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