

Copper Hydride Clusters as Hydrogen Sponges

Summary

For decades hydrogen has been promoted as the fuel of the future. As a transportation fuel, it offers the advantage of having the highest energy output per mass among all competing fuels. Its combustion generates water, making it the most environmentally friendly fuel imaginable.

The storage of hydrogen fuel in solid matrices (metal hydrides sponges) ameliorate the safety issues associated with its flammability and eliminate the need to cool it and compress it into a liquid. However, solid storage materials are costly and prone to decomposition and corrosion.

The purpose of this research project is to use copper, the lightest and most affordable of the noble inert metals, as a hydrogen storage material. Specifically, the following goals are achievable:

Goal No. 1. Synthesis of a nanoscale copper cluster of optimal hydrogen absorptivity, capable of storing and releasing hydrogen in a controllable reversible manner.

Goal No. 2: Chemically stabilize the copper hydride cluster to prevent its decomposition.

Goal No. 3: Measure the efficiency of copper hydride clusters as fuel storage materials.

Background

In 2014, Edwards et al. reported on the synthesis of air-stable copper hydride ion complexes with composition $[\text{Cu}_{28}\text{H}_{15}\text{L}_{12}]\text{PF}_6$ where “L” stands for an organic ligand that stabilizes the central copper core against oxidation.[1] This so-called “Chinese Puzzle Ball” structure is capable of storing fifteen (15) hydride (H⁻) ions that can be released as hydrogen (H₂) fuel by changes in temperature, acidity, or ultraviolet light exposure.

The 28-atom cluster is only one of many structures that may be produced with varied copper composition, including Cu₈ [2], Cu₁₄ [3] Cu₂₀[4], Cu₂₅[5], and Cu₃₂ [6]; recent work in this fertile field, has been summarized by Dhayal, van Zyl, & Liu [7].

As part of the Directed Studies courses offered by the chemistry department, LACC students were able to reproduce the synthesis of the 28-atom cluster and to modify it by changing the protecting ligand [8].

As summarized in the following section, LACC students established a productive collaboration with the University of Texas at San Antonio to extend the characterization of the clusters using mass spectrometry, powder X-Ray Diffraction, Gel Electrophoresis, and Infrared/UV-Vis spectroscopies.

Previous LACC students also confirmed, as documented by Edwards et. al [1] that an obstacle preventing the exploitation of these materials is their tendency to decompose into a much more stable Cu₈HL₆ monohydride fragment, particularly when exposed to fluorescent light and/or acidic conditions. Yet LACC students also confirmed that the larger structure may be regenerated by the addition of hydrogen. This key observation, that the cluster decomposition may be reversed, supports the premise that the copper hydride cluster may be used as hydrogen storage material.

Current research tests the hypothesis that these nano-metal hydride clusters or their stable monohydride fragments can be combined to form much larger structures that may act effectively as hydrogen sponges for fuel storage. The structure of the desired composites will be investigated via electron microscopy and powder XRay diffraction (pXRD) their hydrogen storage capacity will be assessed through Raman infrared and proton nuclear magnetic resonance (1H-NMR) spectroscopies.

Previous Work at LACC

The synthesis of copper hydride clusters involves the controlled reaction of copper(I) cation with lithium borohydride (reducing

agent), in the presence of ligand (protecting agent) in a suitable solvent and under an inert atmosphere (nitrogen gas blanket). Relevant reagents and reaction parameters are summarized in Table 1.

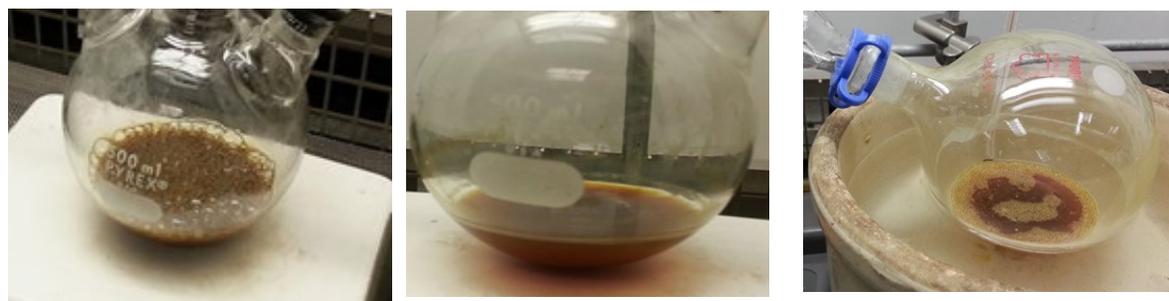
Table 1: synthesis of clusters with thiocarbamate and glutathione ligands.

System	Thiocarbamate
Copper (I) Source	$[(\text{CH}_3\text{CN})_4\text{Cu}]\text{PF}_6$
Ligand	Dibenzyl dithiocarbamate Diethyl dithiocarbamate
Solvent	Tetrahydrofuran
Reducing Agent	Lithium borohydride
Work-up	Methanol wash, Crystallization from DCM
Purification	Liquid Chromatography Size Selecting Precipitation

In a typical reproducible synthesis, 3 mmol of Cu(I) where suspended in 10 mL of THF (Slurry A). A second solution was prepared (B) with 1.2 mmol of ligand and 4 mmol of the lithium borohydride reducing agent dissolved in 30 mL of THF. After the system was evacuated and purged, Slurry A was added via cannula injection to Solution B under a

constant flow of ultra-high purity nitrogen for one to two hours. As summarized in Figure 1, the reaction products may be purified by evaporation of solvent, washing with methanol, and redissolving in dimethylene chloride (DCM), and precipitation with excess methanol to yield an orange/red solid that could be redissolved in DCM and toluene.

Figure 1: Synthesis of CuH clusters protected with dibenzylthiocarbamate ligands.

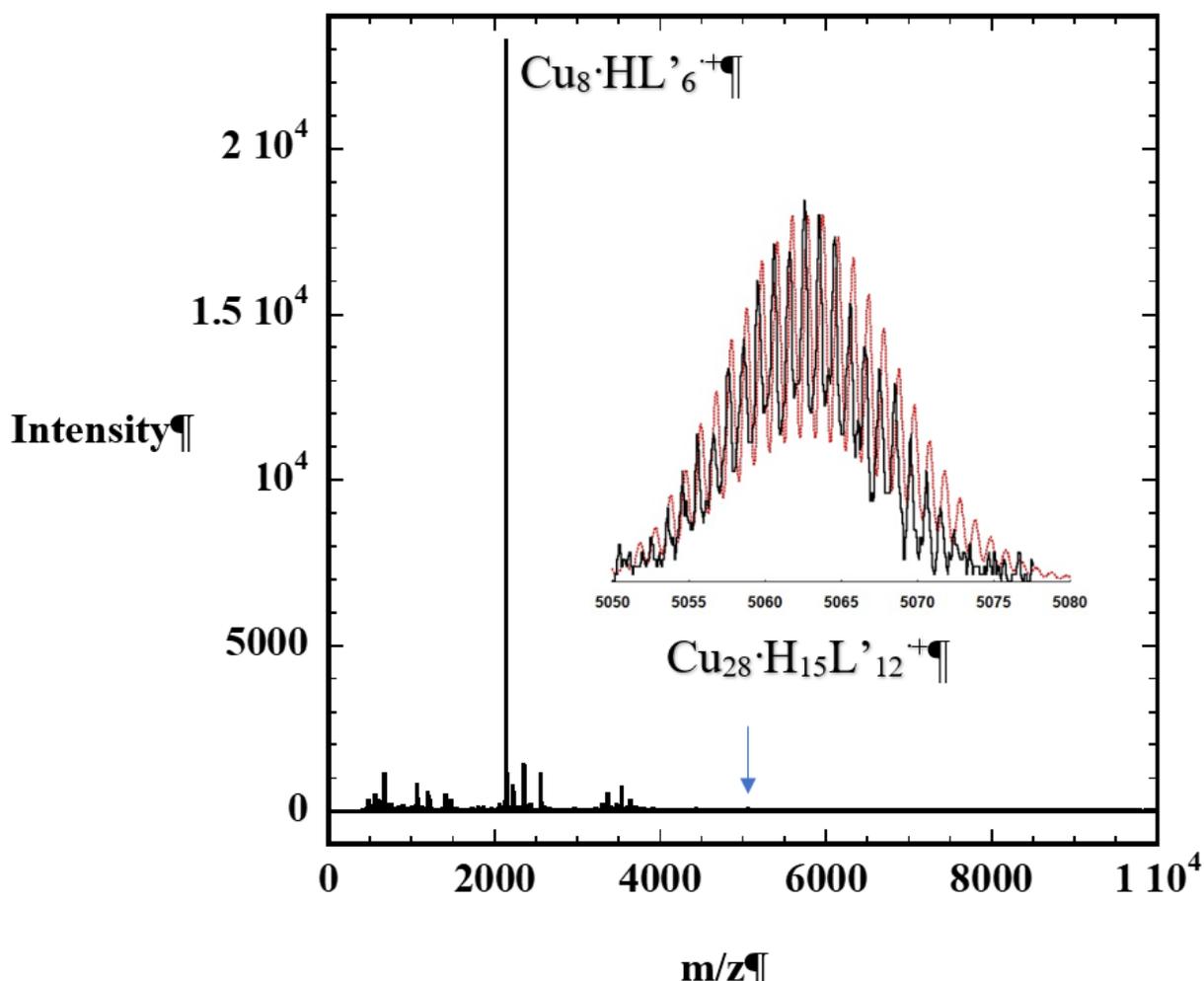




The exploratory reaction produced cluster with a yield of 30% (mp. 230-235 °C). Although the material was air stable in solid form, it was susceptible to decomposition when exposed to sun light and when stored in DCM solution for extended periods of time (days), as judged by its change of color from deep red/orange to yellow (mustard) and olive green. The clusters could be regenerated by addition of excess reducing agent.

Mass analysis of the product at UTSA after several months of storage revealed that $\text{Cu}_8\text{H}_8\text{L}$ is a stable fragment species that dominates the spectra (Figure 2). Results also show the presence of higher-mass clusters although at lower concentrations, manifested as doubly and triply charged species.

Figure 2: ESIMS analysis of CuH clusters showing dominance of Cu_8HL_6 species



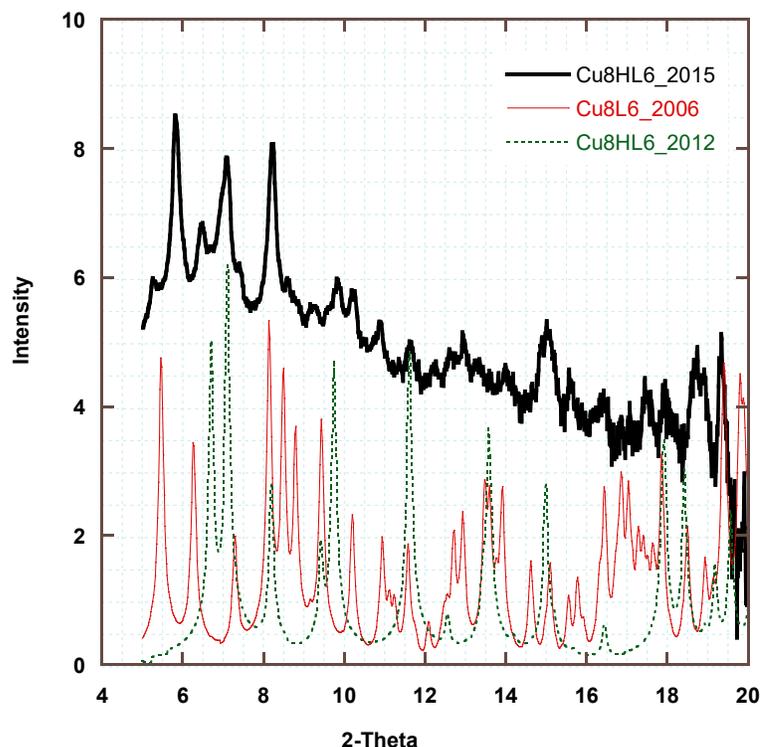
that the hydride may be regenerated in situ by the intentional addition of a hydrogen source

(hydrogen gas, or R_3SiH species) rendering the cluster as hydrogenation catalysts.

Powder samples of CuH clusters were analyzed at UTSA for crystallinity in a pXRD instrument using a narrow slit ($\Delta 2\theta = 0.013$ deg), as summarized in Figure 3, where a geometric

correction ($\sin 2\theta$) has been applied to the intensities.

Figure 3: pXRD spectrograph of the Cu_8HL_6 cage (dark trace) compared to simulated spectra from published single crystal structures of Cu_8L_6 (2012) and the empty Cu_8L_6 with no hydride (2006)



It is clear from the spectrograph that the cluster protected with dibenzyl ligands show long range order and interplanar spacing of a few nanometers. In addition, it is also apparent that the salient features of the pXRD spectrograph may be attributed to contributions from both the monohydride cage and the empty Cu_8 cage.

The structure of the Cu_8HL_6 cage reported by others [7] correspond to a distorted cube

[tetracapped tetrahedral, or bicapped octahedral] with a hydride at the center. Upon loss of the endohedral hydride, the cube becomes well defined by eight copper atoms (one per vertex). One dithiocarbamate binds to each of the six faces of the cube. Both structures are sufficiently different to merit future attempts at separation using LC/MS facilities.

Concluding Remarks

The preliminary results described above show that the copper hydride system offers ample opportunities for further investigations. If the assembly of cluster of corrosion resistant copper cluster of optimal hydrogen absorptivity into a macroscopic hydrogen sponge (by chemical linking) can be realized, then this paves the way their use as transportation fuels.

Ongoing research pursuits the following objectives:

A) Impart coupling functionality to the ligand stabilizing the cluster by attaching a cross-linking carboxylic, amine, organo silane functional group to its terminus.

B) Impart coupling functionality to the cluster: Perform conventional ligand substitution

reactions to impart pre-made clusters with the added functionality.[11] Alternative routes to be studied in parallel are to synthesize the cluster using the functionalized ligands and to modify the ligand while attached to the clusters.

C) Synthesize hydrogen sponges by joining the clusters to each other using conventional protein or organosilane conjugation chemistries.

D) Chemically attach/bind the hydrogen sponge onto bulk metallic substrates to enable its use as fuel storage devices and facilitate heat dissipation during recharging of the sponge.

E) Quantify hydrogen-absorption performance

F) Perform H-D exchange experiments to confirm the hydride count.

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