Aromatic Copper Hydride Cages

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ABSTRACT: Copper clusters are nanoscale materials comprised of a metal core or frame enclosed by a mantle of stabilizing ligands; their exploration offers progress in diverse fields, such as medicine, electronics, and fundamental chemistry as catalysts, reducing agents, corrosion inhibitors, and petroleum sweeteners. When stabilized with dithiocarbamate (DTC) ligands (L), copper clusters show a propensity for reversible hydrogen uptake and a remarkable versatility in size and shape as demonstrated by the facile substitution of the protecting groups and multitude of species attainable. The purpose of this report is to demonstrate the versatility of the Cu-DTC system by the novel use of an aromatic dibenzyl DTC ligand (L') to generate clusters of previously known composition (i.e., Cu4H2L2PF6). As demonstrated herein, the new materials are air-stable and amenable to characterization by high-resolution electrospray ionization mass spectrometry, 1H-nuclear magnetic resonance spectrometry, powder X-ray diffraction, Fourier Transform Infrared Spectroscopy, Ultraviolet-Visible spectroscopy, and Inductively Coupled Plasma Spectrometry. The subject - hydrogen-rich caged cluster materials have potential applications as hydrogen storage sponges to great benefit to material science, energy, and other chemical fields.

KEYWORDS: Copper, Hydrides, Hydrogen storage, Clusters.

INTRODUCTION

For decades, hydrogen has been promoted as the transportation fuel of the future because it has the highest energy output per mass and because of its environmentally friendly combustion products: water [1]. The storage of hydrogen fuel in solid matrices (metal hydrides sponges) ameliorates the safety issues associated with its flammability and eliminates the need to cool it and compress it into a liquid. However, solid storage materials are costly, prone to decomposition, corrosion, and overheating upon recharging [2,3]. Copper, the lightest and most affordable of the noble inert metals, has a peculiar affinity toward hydrides that makes it an ideal candidate for a hydrogen storage material.

The study of copper hydride cages is motivated on the one hand by the versatility of copper organic compounds in organic chemistry, and on the other hand, by the added reactivity associated with large surface areas afforded in small dimensions [4]. At the nanoscale, gold particles are excellent oxidation catalysts facilitating the production of aldehydes, ketones, and epoxides from alkenes [5]. At the molecular level, organocuprates or Gilman reagents are classical carbon coupling reagents [6,7]. Copper hydrides (Stryker reagents) find use as reducing agents and copper halide salts catalyze the hydrolysis of allyl halides [7,8]. Recently, the use of a copper catalyst to promote the asymmetric addition of a hydrogen atom and an amine functional group into an activated internal alkene has been demonstrated [9]. Copper hydride clusters have been shown to catalyze the hydrogenation of ketones to alcohols [10].

Copper cages and inorganic copper clusters and networks have the potential to function as reagents and catalysts because these entities lie in between the molecular and nano-metallic state and their reactivity is largely unexplored and unpredictable. However, unlike gold and silver, copper nanoparticles pose a major synthesis challenge due to their tendency to oxidize upon exposure to air [11]. Recently, Edwards et al. [12] reported on the synthesis of air-stable copper hydride ion complexes with composition [Cu12H12L2]PF6 where “L” stands for dithiocarbamate (DTC) ligand that stabilizes the central copper core against oxida-
tion. This 28-Cu-atom cluster is capable of storing fifteen (15) hydride (H\(_2\)) ions that can be reversibly released as hydrogen (H\(_2\)) fuel by controlled changes in temperature, acidity, or ultraviolet light exposure. The reversibility of the hydrogen charging–discharging process, its chemical stability, and its high thermal conductivity render the copper-hydride cluster a promising material for applications in energy and transportation fields. The so-called Chinese puzzle ball is only one of many hydride structures that may be produced with varied copper composition, including Cu\(_6\) [13–16], Cu\(_{13}\) [17,18], Cu\(_{19}\) [19–22], Cu\(_{23}\) [23], Cu\(_{24}\) [24,25], Cu\(_{26}\) [26,27], Cu\(_{25}\) [25,28,29], Cu\(_{30}\) [10,30], Cu\(_{31}\) [31], Cu\(_{32}\) [32,33], Cu\(_{33}\) [34], and Cu\(_{61}\) [35]. Recent work in this fertile field, including the use of copper hydride compounds as catalyst, has been summarized by several authors [36–41].

The primary objective of the work described here is to demonstrate the versatility of the copper-DTC cluster system by substituting the diisopropyl ligand (L) in a copper monohydride cluster of known composition and structure [20] (Cu\(_8\)HL\(_6^−\)PF\(_6^−\)) with an aromatic dibenzylthiocarbamate ligand (L\′). The aromatic clusters are regenerated upon decomposition by the addition of excess borohydride, a desirable property that can lead to the use of these clusters as hydrogen storage materials. The substitution is significant because it imparts the cluster the rigidity, functionality, and stability associated with aromatic groups while suggesting a plethora of other similar substitutions. The new materials are selectively characterized by high-resolution electrospray ionization mass spectrometry (ESIMS), proton nuclear magnetic resonance (\(^1\)H-NMR) spectrometry, powder X-ray diffraction (pXRD), Fourier Transform Infrared Spectroscopy (FTIR), Ultraviolet-Visible spectroscopy, and Inductively Coupled Plasma Spectrometry (ICP).

RESULTS AND DISCUSSION

The synthesis of copper hydride compounds involves the controlled reaction of copper(I) cation with a reducing agent (lithium borohydride), in the presence of a ligand (protection agent) in a suitable solvent (Tetrahydrofuran) and under an inert atmosphere (Nitrogen gas blanket). Details are provided in the Supplementary Material. In practice, a multitude of products with varying copper to ligand composition is produced depending on the ligand to copper ratio and other reaction conditions, as testified by the broad list of published structures from the above synthetic approach [20,24,28,30,32,36].

Mass analysis of the product after several months of storage revealed that Cu\(_8\)HL\(_6^−\)PF\(_6^−\) is a stable fragment species that dominates the spectra Figure 1, as previously reported.\(^{20}\)

The inset in Figure 1 represents an isotopic fit of the ESIMS envelope by a singly charged Cu\(_8\)HL\(_6^−\) fragment, demonstrating that the spectrometer can resolve the complications posed by the existence of two copper isotopes. More significantly, the isotopic fit demonstrates the presence of a hydride in the Cu\(_8\)HL\(_6^−\)PF\(_6^−\) cage in accordance with pXRD and 1H-NMR results.

Higher-mass clusters are observable at apparent lower concentrations as doubly and triply charged species (Figure 2) by tuning the parameters of the mass spectrometer.

As is typical of electrospray mass spectra, a number of peaks are apparent in the spectra of Figure 2, most probably associated with multiply charged states of the same species, adducts, and mild fragmentation products of the ionization process. A detailed discussion of each component is beyond the scope of this report that focuses on the abundance and special stability of the Cu\(_8\)HL\(_6^−\) cluster. A major shortfall of the ESIMS technique is that it may be biased to species that are easily ionizable and it may be the case that the overwhelming abundance of the Cu\(_8\)HL\(_6^−\) species in Figures 1 and 2 is partly due to this bias in detection. Indeed, the abundance of the parent [Cu\(_8\)HL\(_6^−\)PF\(_6^−\)] species in the freshly synthesized material is supported by elemental analysis (Table 1).

The experimental Cu/S ratio (1.1) is consistent with the presence of the larger [Cu\(_8\)HL\(_6^−\)L\(_{12}\)]PF\(_6^−\) (1.2) species in the freshly synthesized product over that of the Cu\(_8\)HL\(_6^−\)PF\(_6^−\) cage (0.67).

Although the freshly prepared material is air-stable in solid form, it is susceptible to decomposition when exposed to sunlight and when stored in dichloromethane solution for extended periods of time (days), as judged by its change of color from deep red/orange to yellow (mustard) and olive green. However, the clusters could be regenerated by the addition of excess reducing agent.

Powder samples were analyzed 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.

It is clear from the spectrograph that the clusters 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. Indeed, efforts to extract cell parameters using CMPR—a free access software [42] favored large orthorhombic cells must likely enclosing four cages (a =37.96°A, b = 50.50°A, c = 13.6°A; α−−β−−δ = 90°). As suspected from the presence of at least two structures, the Figure of Merit of 4.8 is low, given that a value of 10 represents a threshold value [43]. The structure of the Cu 8 HL 6 PF 6 cage reported by others [36] corresponds 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. It is conceivable that the hydride may be also be regenerated in situ by the intentional addition of a hydrogen source (hydrogen gas or R 3 SiH species) rendering the clusters as hydrogenation catalysts and hydrogen storage sponges.

According to Edwards’s et al. [12], the hydride in the Cu 8 HL 6 PF 6 species with diisopropyl ligands would appear around 7.05 ppm. Given the fact that the phenyl hydrogens of L’, L’= S 2 CN(CH 2 ) 2 (C 6 H 5 ) 2 are in the range of 7.00–7.5 ppm, the hydride in the 1H NMR spectrum will be hard to detect. However, the integration ratios of L’ in that region are theoretically 5:2, while the observed integration ratios (Figure 4) of the Cu 8 HL 6 species are slightly higher than the 5:2 ratio which could suggest that the hydride of Cu 8 HL’ 6 PF 6 is imbedded in the phenyl area.

The phenyl hydrogens and the methylene group were shifted from 7.29 to 7.11 ppm and 5.24 to 5.29 ppm, respectively, which supports the assumption of L’ being bonded to a copper core as detailed in the Supplementary Material.

A shift in frequencies of key vibrational modes of the ligand was observed by FTIR (Supplementary Material).
Most notably, a blue shift in the v_{CSS} vibration from 990 to 1,000 cm⁻¹ and the existence of a single band in that region is consistent with dibenzyldithiocarbamate anchoring to the copper cage as a bidentate ligand [44].

The optical spectra of the cluster (Figure S6 of the Supplementary Material) is dominated by three bands in the ultraviolet region (255, 295, and 350 nm) typical in dithiocarbamate ligands [45], and an onset of absorption in the visible at 500 nm. There is no evidence for a local surface plasmon band indicative of metal nanoparticles are fine structure of larger molecular clusters [46]. Lower nuclearity clusters such as Cu_{14}HL_6 PF_6 have been shown to be fragmentation products of larger clusters [12] and thus are more stable. As such, it is suggested that the added functionality of the substitutions reported here may be exploited to chemically link smaller clusters into a larger, rigid network that may be used as a robust hydrogen storage sponge.

CONCLUSION

The results described above show that cluster hydride materials allow the substitution of different functional groups while retaining well-known stable compositions. These new materials offer ample opportunities for further investigations which may include even larger clusters or cluster networks, of well-known composition and structure, that are copper-rich but in addition to hydrides may incorporate other lighter alloys or intermetallic phases. For example, a copper analog of the famous A_{24}X_{60} clusters, wherein normally A = Au or dopant (Ag, Cu, Pd . . .) atoms and X = ligand, would be of great interest. Ongoing research on this subject pursues the following objectives:

A) Impart coupling functionality to the ligand stabilizing the cluster by attaching a cross-linking carboxylic, amine, organosilane 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 [29]. 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 and perform H-D exchange experiments to confirm the hydride count.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interest pertaining this publication.

SUPPLEMENTARY MATERIAL

Experimental procedures and characterization data for all new compounds.

REFERENCES


SUPPLEMENTARY INFORMATION

Graphical TOC Entry

METHODS

When producing copper-hydride compounds, the synthesis was performed in tetrahydrofuran using Tetrakis(acetonitrile)copper(I) hexafluorophosphate as the Cu+ source and sodium dibenzyldithiocarbamate as the stabilizing ligand.

Relevant reagents and reaction parameters are summarized in Table S1.

In a typical reproducible synthesis, 3 mmol of Cu(I) were 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 DCM, and precipitation with excess methanol to yield an orange/red solid that could be redissolved in dichloromethane (DCM) and toluene. The exploratory reaction produced clusters with a yield of 30 % (mp. 230-235°C).

Composition was probed via ESI-MS, NMR, and Elemental Analysis. Size and structure were assessed via powder X-Ray Diffraction.

Table S1. Starting reactants for the synthesis of CuH materials.

<table>
<thead>
<tr>
<th>System</th>
<th>CuHCCC</th>
<th>Molar Quantities</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper(I) Source</td>
<td>[Cu(CH, CN),]PF6</td>
<td>3 mmol</td>
</tr>
<tr>
<td>Ligand</td>
<td>Dibenzylidithiocarbamate</td>
<td>1.2 mmol</td>
</tr>
<tr>
<td>Solvent</td>
<td>Tetrahydrofuran</td>
<td>40 mL</td>
</tr>
<tr>
<td>Reducing Agent</td>
<td>Lithium borohydride</td>
<td>4 mmol</td>
</tr>
<tr>
<td>Work Up</td>
<td>Methanol wash, Crystallization from DCM</td>
<td></td>
</tr>
</tbody>
</table>

PROTON NUCLEAR MAGNETIC RESONANCE CHARACTERIZATION

The phenyl hydrogens and the methylene group were shifted from 7.29 ppm to 7.11 ppm and 5.24 ppm to 5.29 ppm respectively which can be given credit to L' being bonded to a copper core. The theoretical integration ratios are 4:2:4 for the ortho, para, and metal hydrogens, respectively. The para hydrogen is merged into the ortho or meta regions which then yield two regions.[1] Region A has an area of 5 while the area of region B has an area of 6 in respect to the methylene hydrogens. Given that the total area has an integration value of 11 we can extrapolate that a hydride is in region B. From the mass spectrum the abundance of the [Cu28H15L'12]PF6 cluster is small compared to Cu8HL'6 PF6 cage. Hence the signals near: 4.20, 1.25, and -0.85 ppm for the [Cu28H15L'12]PF6 hydrides are not noticeable.

MASS SPECTROMETRY ANALYSIS

Mass analysis were performed on a Bruker microOTOF time-of-flight mass spectrometer with an electrospray ionization source (ESI-MS) using toluene as a solvent. Key operational parameters are summarized below. Isotopic fits to experimental envelopes were performed using mMass - open source mass spectrometry tool.[2]

FTIR Characterization

Raw ligand and product were analyzed as compressed powders in a Perkin Elmer Spectrum 100 FTIR spectrometer equipped with an ZnSe ATR accessory. After exhaustive purification, the product shows pronounced IR absorption at 1483 cm⁻¹ characteristic of νC-N vibrations with partial double bond character in metal dithiocarbamate complexes (Figure S5).[2] It should be noted that the band is red shifted relative to the starting sodium dibenzylidithiocarbamate stock (1493 cm⁻¹). Also noteworthy is the blue shift in νC-SS vibration in the cluster (1000. cm⁻¹) relative to the free ligand (990 cm-1).[4] The blue shift is consistent with a shift from antisymmetric to symmetric vibrational mode associated with a bidentane ligand.[5]

Aromatic νC-H modes are observed at 3030 and 3068 cm⁻ are only slightly red. The shifting of spectral bands depicted
**Table S2. Key electrospray ionization mass spectrometer parameters.**

<table>
<thead>
<tr>
<th>Source</th>
<th>Ion Optics</th>
<th>Time of Flight TOF</th>
<th>Processing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>ESI</td>
<td>Capillary Exit 200.0 V</td>
<td>Corrector Fill 40 V</td>
</tr>
<tr>
<td>Focus</td>
<td>Not active</td>
<td>Capillary Exit 200.0 V</td>
<td>Corrector Fill 40 V</td>
</tr>
<tr>
<td>Scan Begin</td>
<td>50 m/z</td>
<td>Hexapole 1 25.0 V</td>
<td>Pulsar Push 770 V</td>
</tr>
<tr>
<td>Scan End</td>
<td>2000 m/z</td>
<td>Hexapole 2 28.1 V</td>
<td>Pulsar Push 770 V</td>
</tr>
<tr>
<td>Ion Polarity</td>
<td>Positive</td>
<td>Hexapole 2 27.0 V</td>
<td>Flight Tube 8600 V</td>
</tr>
<tr>
<td>Capillary</td>
<td>4500 V</td>
<td>Hexapole RF 800. V</td>
<td>Corrector Extract 467 V</td>
</tr>
<tr>
<td>End Plate Offset</td>
<td>-500 V</td>
<td>Transfer Time 225.0 µS</td>
<td>TOF Detector 2100 V</td>
</tr>
<tr>
<td>Nebulizer</td>
<td>1.0 Bar</td>
<td>Pre-Pulse Storage Time 43 µS</td>
<td>TOF Detector 2100 V</td>
</tr>
<tr>
<td>Dry Heater</td>
<td>145 oC</td>
<td>Lens1 Storage 50.0 V</td>
<td>C0 201.4898</td>
</tr>
<tr>
<td>Dry Gas</td>
<td>5.0 mL/min</td>
<td>Lens 1 Extraction 27.3 V</td>
<td>C1 405780.03</td>
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<tr>
<td>Divert Valve</td>
<td>Source</td>
<td>Lens 2 9.8 V</td>
<td>C2 0</td>
</tr>
<tr>
<td></td>
<td>Source</td>
<td>Lens 3 −30.2 V</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Source</td>
<td>Lens 4 0.0 V</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Source</td>
<td>Lens 5 −40.0 V</td>
<td></td>
</tr>
</tbody>
</table>

**Figure S1.** Synthesis of CuH clusters protected with dibenzylthiocarbaminate ligands.
in Figure S5 is significant because it shows that the signal is NOT due to excess ligand unbound to the cluster.

**UV-VIS Characterization**

The optical spectra of the product (Figure S6) was measured from 240 nm – 800 nm in a Beckman D800 spectrophotometer using Tetrahydrofuran (THF) as a solvent. The scan started at 240 nm to avoid solvent interference (cut-off frequency of 220 nm). The ultraviolet region of the spectrum is dominated by three bands arising from transitions in the the ligand.[6] The bands at 255nm and 295 nm are due to transitions in the thiocarbonyl group. The salient hump at 350 nm is associated with bonding to nonbonding (n → π*) transitions of electrons in one of the sulfur atoms.[6] The visible region shows a monotonously decaying signal responsible for the amber hue of dilute solutions. An onset of absorption at 500 nm (~ 2.7 eV) is apparent when the absorbance is plotted against photon energy (eV) and the absorbance is scaled as 1/E2 to facilitate comparison to absorption by bulk gold.[7,8]
Figure S5. Comparison of FTIR spectral features of product (green trace) to sodium dibenzylidithiocarbamate hydrate (red trace). The spectra of the ligand has been displaced vertically for ease of comparison.

Figure S6. UV-Vis Spectra of Copper Hydride Cluster.
REFERENCES


Figure S7. Optical Absorption of Cu-H cluster (red solid trace) compared to spectral features of bulk gold (green dotted trace).