Copper Hydrides

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# Chinese Puzzle Molecule: A 15 Hydride, 28 Copper Atom Nanoball**

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**Abstract:** *The syntheses of the first rhombicuboctahedral copper polyhydride complexes $[Cu_{28}(H)_{15}(S_2CNR)_{12}]PF_6$ ($NR = N^nPr_2$ or aza-15-crown-5) are reported. These complexes were analyzed by single-crystal X-ray and one by neutron diffraction. The core of each copper hydride nanoparticle comprises one central interstitial hydride and eight outer-triangular-face-capping hydrides. A further six face-truncating hydrides form an unprecedented bridge between the inner and outer copper atom arrays. The irregular inner $Cu_4$ tetrahedron is encapsulated within the $Cu_{24}$ rhombicuboctahedral cage, which is further enclosed by an array of twelve dithiocarbamate ligands that subtends the truncated octahedron of 24 sulfur atoms, which is concentric with the $Cu_{24}$ rhombicuboctahedron and $Cu_4$ tetrahedron about the innermost hydride. For these compounds, an intriguing, albeit limited, $H_2$ evolution was observed at room temperature, which is accompanied by formation of the known ion $[Cu_8(H)(S_2CNR)_6]^+$ upon exposure of solutions to sunlight, under mild thermolytic conditions, and on reaction with weak (or strong) acids.*

Copper hydride was the first described binary transition-metal hydride[1] and has subsequently been reported to possess a range of interesting physical properties. Later studies[2] revealed our limited understanding of the properties of such hydrides, even for this simple and long-known binary compound.[3] The well characterized copper hydride containing Stryker reagents are catalytically applicable to C–F bond activation,[4] reductions, and hydrogenations[5] and have been the subject of thorough studies including a significant recent refinement of the understanding of the nature of the hydrides lying on the outside of the six copper octahedral array based on neutron spectroscopy methods.[6]

Our studies of anion coordination environments in chalcogen-stabilized copper cluster compounds led us to the previously described $Cu_7$ and $Cu_8$ complexes, which contain a single hydride within each cluster molecule.[7,8] Remarkably, on treatment with excess borohydride, a significant expansion of the nuclearity together with substantial capture of hydride was observed for either of these clusters to yield a molecule that contains 15 hydrides and 28 copper atoms, namely $[Cu_{28}(H)_{15}(S_2CNR)_{12}]PF_6$ (for $\mathbf{1_H}$: $NR = N^nPr_2$; for **2**: NR = aza-15-crown-5). More recently, a similar expansion of nuclearity along with an increase in the hydride to copper ratio has been described.[9] The $Cu_{28}H_{15}$ cluster cations are air- and moisture-stable both in the solid state and in solution. Their structure is best understood in terms of concentrically arranged layers of atoms that form well understood regular geometric arrangements.[10] The metal hydride array contains two types of copper atoms: an inner tetrahedron and those of the outer rhombicuboctahedral array [an Archimedean polyhedron[11] with 24 vertices that comprises eight triangular faces and eighteen square faces ($8_3 + 12_4 + 6_4$) with $O_h$ symmetry[12] in its most regular presentation]. In the cubic structure that was observed for $\mathbf{1_H}$, this idealized geometry is approached, whereas in the triclinic structure of **2** a slightly less regular but clearly rhombicuboctahedral arrangement was found. The hydrides are of three chemical/structural types, with one type occupying two distinct crystallographic sites.

The two compounds $\mathbf{1_H}$ and **2** were characterized by X-ray diffraction[13] (Figure 1; see also the Supporting Information, Table S1–S3), neutron diffraction ($\mathbf{1_H}$; Figure S1, Tables S4 and S5), and a broad set of standard chemical characterization methods, including elemental analysis, NMR spectroscopy, ESI mass spectrometry ($\mathbf{1_H}$; Figures S2 and S3) and energy dispersive X-ray spectroscopy (EDS) to determine the Cu/S atomic ratio ($\mathbf{1_H}$; Figure S4, Table S6). The positive-ion ESI mass spectrum of $\mathbf{1_H}$ clearly displays a prominent band for the molecular ion $[Cu_{28}(H)_{15}(S_2CN^nPr_2)_{12}]^+$ ($[\mathbf{1_H}]^+$) at $m/z$ 3910.1 (calcd 3910.3), and its theoretical isotopic pattern matches well with the experimental observations (Figure S2). The mass difference for the deuterium analogue $[\mathbf{1_D}]^+$ ($[Cu_{28}(D)_{15}(S_2CN^nPr_2)_{12}]^+$; $m/z$ 3923.6), reveals the incorporation of more than 13 hydrides per cluster (Figure S3); this value is lower than the 15 hydrides that would be expected for ultrapure borodeuteride, but consistent with the stated

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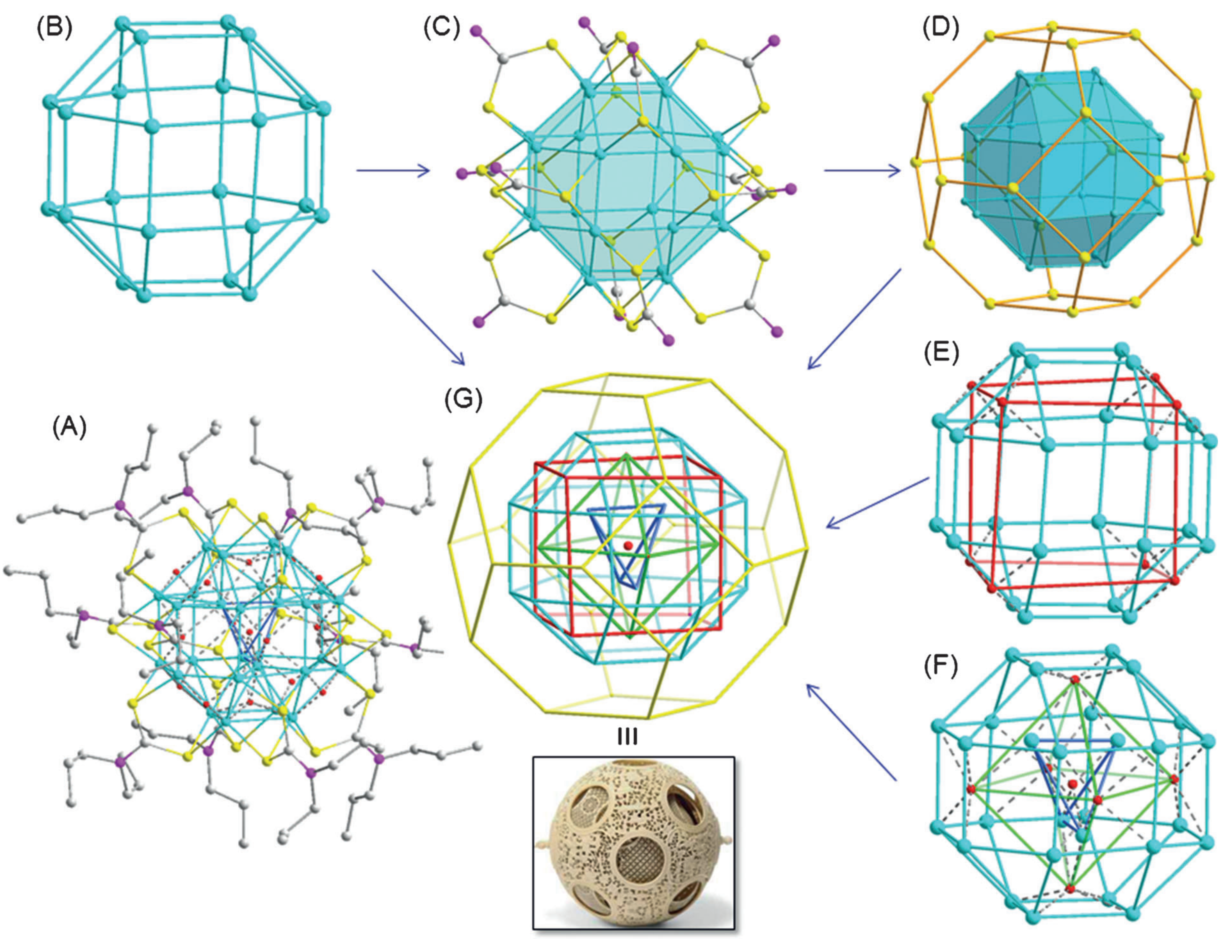

*Figure 1.* A) The cubic $[Cu_{28}(H)_{15}\{S_2CNPr_2\}_{12}]$ cation. B) The rhombicuboctahedral framework of 24 Cu atoms. C) Each of the twelve square faces of the $Cu_{24}$ core is capped by a dtc ligand. D) The $Cu_{24}$ core is enclosed by a truncated octahedron of 24 sulfur ligands. E) Three-coordinate hydrides ($\mu_3$-H) on eight triangular faces of the $Cu_{24}$ core. F) Six truncating hydrides inside six square faces of the $Cu_{24}$ core form a bridging octahedron motif; the core is concentrically arranged around the interstitial hydride ($\mu_4$-H). G) The core assembly: $H@Cu_4$(tetrahedron)@$H_6$(octahedron)@$Cu_{24}$(rhombicuboctahedron)@$H_8$(cube)@$S_{24}$(truncated octahedron) reminiscent of a Chinese puzzle ball (inset). Carbon gray, copper cyan, hydrogen red, nitrogen pink, sulfur yellow.

modest purity of the commercially available borodeuteride reagent.

X-ray diffraction studies revealed that the cluster core elements of $\mathbf{1_H}$ and **2** are isostructural. Only the architecture of $\mathbf{1_H}$, which bears 28 copper atoms, 15 hydrides, and 12 dtc ligands (dtc = di-*n*-propyldithiocarbamate = $S_2CN^nPr_2$; Figure 1 A) is discussed in detail alongside the corresponding results for $\mathbf{1_H}$ that were obtained neutron diffraction. The X-ray diffraction study of $\mathbf{1_H}$ revealed that the cation contains 24 copper atoms that form a slightly distorted rhombicuboctahedron (Figure 1 B) in which Cu–Cu separations (2.603(1) to 2.824(1) Å) lie clearly within the range reported for $[Cu_8(H)(S_2CN^nPr_2)_6]^+$ (**3**; 2.576(1)–2.989(2) Å).[7d] Twelve square faces of the rhombicuboctahedron share edges with two triangles and two squares, and these are bridged by a dtc ligand that bridges four metal centers in a ($\mu_2$, $\mu_2$) binding mode outside the rhombicuboctahedron (Figure 1 C). The 24 sulfur atoms thus form a truncated octahedral cage (Figure 1 D). The Cu–S bond lengths average 2.354 Å and are comparable to the Cu–S distance in **3** (with an average of 2.314 Å) with a similar ligand S⋯S bite distance of 3.059 Å. Within the cluster, electron and nuclear densities were observed to be centered about twelve sites that form a cuboctahedron within the $Cu_{24}$ skeleton and are consistent with the electron and nuclear densities that would be expected for a copper occupancy of one third. These twelve sites are best described as the sum of the densities of three mutually perpendicular pairs of inversion-related tetrahedra lying about the crystallographic inversion center (for the cubic structure, this center also coincides with the intersection of the three-fold rotation axes; Figure S5). The significantly higher anisotropic displacement ellipsoids that were refined from the X-ray data for these inner twelve sites and modelled to one-third copper occupancy are in contrast to the typical pattern of displacement parameters for like atoms, which become smaller the closer to the center of a molecule the atoms lie. Furthermore, these parameters are not inconsistent with models that invoke significant deviation from the modelled average site through either dynamic and/or static disorder processes. The description of the four Cu atoms as constituting a tetrahedron is strongly reproducible by DFT calculations on the $[Cu_{28}H_{15}(S_2CNH_2)_{12}]^+$ model. Several structures that are fully or partly consistent with the crystal disorder have been tested by geometry optimization. Calculations indicate a clear energetic minimum for a tetrahedral structure of the central $Cu_4$ unit, with a full molecular structure of $D_{2d}$ symmetry characterized as a true minimum by frequency calculations (Figure S6). These calculations also indicate a significant level of tolerance to a range of distortions within the $Cu_{28}H_{15}$ core assembly; in particular, some distortion of the overall geometry of the $Cu_{24}$ rhombicuboctahedron away from the strictly regular configuration appears to cost little in terms of energy.

The metric parameters of the DFT-optimized structure are in satisfying agreement with experimental results obtained by X-ray and neutron diffraction (Table S7). The average Cu–Cu distance (2.644 Å) in the tetrahedron is shorter than the sum of the van der Waals radii for copper atoms (2.80 Å). The average Cu–Cu distance in the square faces of the rhombicuboctahedron about the pseudo $C_4$ axes (2.65 Å) is marginally shorter than for the square faces about the pseudo $C_2$ axes (2.67 Å). Therefore, to the best of our knowledge, $\mathbf{1_H}$ and **2** represent the first clusters with a generalized rhombicuboctahedral structure (Figure S7).[12] The diameter of the approximately spherical unit ($CH_3\cdots CH_3$) in $\mathbf{1_H}$ is 19.81 Å, which falls in the range of small nanoparticles; the spherical unit is thus of similar size to the recently reported thiolate- and phosphine-protected (Cu, Ag, and Au) nanoclusters that were fabricated by similar borohydride reductions.[9,14,15]

The $^1H$ NMR spectrum of $\mathbf{1_H}$ exhibits three broad singlet hydride resonances at 4.20, 1.25, and −0.81 ppm with an integration ratio of 6:1:8 (Figure S8). These values were clearly confirmed by $^1H$ and $^2H$ NMR spectroscopy of the deuterium-labeled analogue $\mathbf{1_D}$ (Figures S9 and S10), and indeed, the two resonances of lower intensity were first located in the NMR spectrum of deuterium-labeled compounds subsequent to the characterization of the hydrides inside the rhombicuboctahedron by neutron diffraction. Neutron diffraction of $\mathbf{1_H}$ (Figure S1) clearly defined the positions of the 15 hydrides of the $Cu_{28}H_{15}$ copper hydride core: 1) Eight three-coordinate ($\mu_3$-H) hydrides cap each of the eight triangular faces of the $Cu_{24}$ rhombicuboctahedron (Figure 1E); these eight hydrides lie on two different crystallographic sites: Two hydrides lie on the three-fold rotation axis, and the remaining six hydrides are described by a single general position. 2) Six square-face-truncating hydrides[16] (Figure 1F) fall into two sets with respect to occupancy of a unique set of inner $Cu_4$ atomic sites: four five-coordinate ($\mu_5$-H) hydrides (4 Cu atoms of the outer square and 1 Cu atom of the inner tetrahedron) and two ($\mu_6$-H) hydrides that are coordinated to six copper atoms (4 Cu atoms of the square and 2 Cu atoms of the inner tetrahedron). 3) One four-coordinate ($\mu_4$-H) hydride is found in tetrahedral geometry at the cluster center.

The ($\mu_3$-H) hydrides lie above the $Cu_3$ planes at a distance between 0.60(4) and 0.70(2) Å, the truncating hydrides are inside the $Cu_4$ squares by 0.58(2) Å. The truncating hydrides exhibit a substantial range in Cu–H distances to the atoms of the square faces from 1.86(3) to 2.12(3) Å and a similarly broad range of 1.77(4) to 2.01(5) Å for the distances to the inner copper atoms. The average bond length, 1.70 Å, of (Cu-$\mu_3$-H) is comparable to the length of 1.76(3) Å that was reported for $[Cu_6(P(p\text{-tolyl})_3)(\mu_3\text{-H})]_6$.[6] The average bond length for (Cu-$\mu_4$-$H_{central}$) of 1.56(5) Å is considerably shorter than the 1.86(2) Å of $[Cu_4(\mu_4\text{-H})(\mu_3\text{-Cu})_3\{S_2C(\text{aza-15-crown-5})\}_6]$.[7d] All inner copper atoms are thus coordinated to three hydrides each, whereas each copper atom of the $Cu_{24}$ shell has a distorted tetrahedral $S_2H_2$ coordination sphere. These hydride locations were fully reproduced by DFT calculations (Table S7). To the best of our knowledge, these are the first metal clusters that simultaneously involve capping ($\mu_3$-H), truncating ($\mu_5$-H, $\mu_6$-H), and interstitial hydrides ($\mu_4$-H). The structure of $\mathbf{1_H}$ displays a geometric entity that is reminiscent of a Chinese puzzle ball and can be expressed concentrically as H(center)@$Cu_4$(tetrahedron)@$H_6$(octahedron)@$Cu_{24}$(rhombicuboctahedron)@$H_8$(cube)@$S_{24}$(truncated octahedron) (Figure 1G), to generate an aesthetically pleasing structure hitherto unknown in cluster chemistry.

As the $C_3$ axes of the postulated sets of central $Cu_4$ tetrahedra are not co-linear with the three-fold axis of the $Cu_{24}$ rhombicuboctahedron, the observed symmetry of individual $\mathbf{1_H}$ molecules is $D_{2d}$. For the static case, the $^1H$ NMR spectrum of the $Cu_{28}$ clusters should comprise peaks with integration ratios of 4:4:2:2 for the twelve dtc ligands and 4:2 for the six truncating hydrides, but no such splitting patterns were observed even at low temperature (Figure S11). We propose that on the NMR time scale, a rapid reorientation process occurs during which the four inner copper atoms switch between the six possible tetrahedral sets that constitute the experimentally observed cuboctahedral electron and nuclear density distributions (Figure S12). The well characterized mobility of H atoms in bulk metal hydrides[17] could also be consistent with the proposal that all of the inner hydrides are involved in a fluxional process together with the inner array of four copper atoms.

Hydrogen evolution experiments were undertaken on solutions of $\mathbf{1_H}$ under conditions of solar irradiation,[18] thermolysis, and acidification (Figure 2). Variable-temperature (VT) $^1H$ and $^2H$ NMR studies in $CDCl_3$ $\{CHCl_3\}$ showed that $\mathbf{1_H}$ $\{\mathbf{1_D}\}$ decomposed to **3** with liberation of $H_2$ ($\delta = 4.61$ ppm) $\{D_2, \delta = 4.59$ ppm$\}$ upon heating from 70 to 80 °C

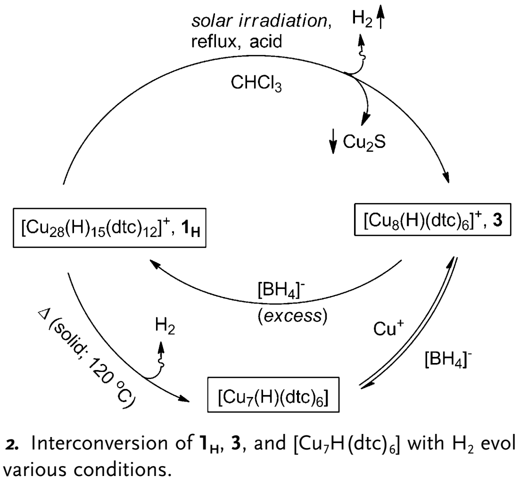

*Figure 2.* Interconversion of $\mathbf{1_H}$, **3**, and $[Cu_7H(dtc)_6]$ with $H_2$ evolution under various conditions.

for 20 minutes (Figures S13 and S14), with concomitant deposition of $Cu_2S$ at the bottom of the NMR tube, which was confirmed by SEM and EDS analyses (Figure S15, Table S6). Similarly, $\mathbf{1_H}$ liberated $H_2$ on solar irradiation for one hour, and fully decomposed to **3** in the next two hours while the temperature rose to approximately 44 °C (Figure S16). The $H_2$ evolution rate is therefore slower under sunlight irradiation than under thermolysis. $H_2$ liberation was confirmed by a gas chromatograph equipped with a thermal conductivity detector (TCD). Compound $\mathbf{1_H}$ is capable of releasing 4.0, 2.6, 2.0, and 12.2 equivalents of $H_2$ per molecule at a temperature above 70 °C (reflux), when exposed to solar energy, in the presence of weak acid (acetic acid), and strong acid (HCl), respectively, while decomposing to **3**. After $H_2$ evolution, **3** can be returned to $\mathbf{1_H}$ by treatment with $[BH_4]^-$ in 71 % yield (Figure 2). For completeness, $\mathbf{1_D}$ was also reacted with HCl in the NMR tube, and a triplet at 4.58 ppm and a doublet at 4.70 ppm were observed in the $^1$H NMR and $^2$H NMR spectra, respectively (Figures S17 and S18), which clearly demonstrates the truly hydridic state of the hydrogen atoms of the metal hydride core. In the solid state, the cluster $\mathbf{1_H}$ decomposed to $[Cu_7H(dtc)_6]$ with liberation of one equivalent of $H_2$ per molecule (by GC) above 120 °C. $[Cu_7H(dtc)_6]$ and **3** were able to interconvert through the reaction of one equivalent of the cationic copper species and the $[BH_4]^-$ salt, respectively.[8d] Interconversion of $\mathbf{1_H}$ into **3** or $[Cu_7H(dtc)_6]$ with concomitant release of $H_2$ was readily demonstrated under mild conditions.

The intriguing structural features of this molecule and its facile assembly and disassembly with release of hydrogen in the absence of any catalytic activity provides fascinating insights into the unsuspected structural potentialities of hydride—the smallest anion. The facile expansion of cluster nuclearity upon reaction of the $Cu_8$ complex with borohydride suggests a significant role for hydride in the formation of higher-nuclearity cluster compounds of copper and other metals, especially for cluster compounds of gold and silver. Although the 44 silver atom nanocluster compounds of Zheng and co-workers[14b] and the gold clusters of the groups of Kornberg[15a] and Murray[15d] have been carefully characterized by X-ray crystallography, hydrides were not postulated to be present in the vicinity of such heavy atoms, and when an adequate fit to the data had been achieved, modelling was terminated. The presence of external bridging staple motifs around each of these structures is noted, and a comparison with the ($\mu_2$, $\mu_2$) dithiocarbamate binding of $\mathbf{1_H}$ and **2** is drawn.

The geometry of the silver and gold clusters that are based on icosahedra or Marks decahedra conform more closely to the proposals of MacKay[19] in terms of the geometric features for a close-packed arrangement of a relatively small numbers of spheres, whereas molecules $\mathbf{1_H}$ and **2** exemplify a novel manner of achieving a relatively high packing density for an approximately spherical distribution of atoms. The density of the $Cu_{28}H_{15}$ cores of $\mathbf{1_H}$ and **2** has been calculated for a selection of limiting surfaces with choices of spheres with various radii enclosing the core and lying between the $H_{cap}$ and S arrays (Figure S19). The density of the core for a radius chosen midway between the outer hydride and sulfur arrays is intermediate between that of bulk copper metal and bulk copper hydride. Therefore, these structures are clearly copper hydride nanoclusters that are quite distinct from previously reported molecular structures for which a rhombicuboctahedral array of metal atoms that was constructed using covalent linking groups yielded open molecular nanoball structures.[20]

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