

A Nanospheric Polyhydrido Copper Cluster of Elongated Triangular Orthobicupola Array: Liberation of H₂ from Solar Energy

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S Supporting Information

ABSTRACT: An unprecedented air-stable, nanospheric polyhydrido copper cluster, [Cu₂₀H₁₁(S₂P(OⁱPr)₂)₉] (**1_H**), which is the first example of an elongated triangular orthobicupola array of Cu atoms having C_{3h} symmetry, was synthesized and characterized. Its composition was primarily determined by electrospray ionization mass spectrometry, and it was fully characterized by ¹H, ²H, and ³¹P NMR spectroscopy and single-crystal X-ray diffraction (XRD). The structure of complex **1_H** can be expressed in terms of a trigonal-bipyramidal [Cu₂H₅]³⁻ unit anchored within an elongated triangular orthobicupola containing 18 Cu atoms, which is further stabilized by 18 S atoms from nine dithiophosphate ligands and six capping hydrides. The positions of the 11 hydrides revealed by low temperature XRD were supported by a density functional theory investigation on the simplified model [Cu₂₀H₁₁(S₂PH₂)₉] with C_{3h} symmetry. **1_H** is capable of releasing H₂ gas upon irradiation with sunlight, under mild thermal conditions (65 °C), or in the presence of acids at room temperature.

Transition-metal hydride complexes are attractive because of their fascinating structural and bonding aspects for synthetic and theoretical chemists^{1,2} and also play an important role as key intermediates in various heterogeneous and homogeneous catalyses³ with significant contributions in hydrogen storage.⁴ Copper hydride, a hexagonal Wurtzite-type structure,⁵ was the first reported binary metal hydride.⁶ Its application in hydrogen storage technology is limited by its pyrophoric nature, as it decomposes above -20 °C. Subsequently, efforts have been directed to the development of various Cu(I) hydrido complexes with lower (mono-, di-, or trinuclear) or higher (hexa- or octanuclear) nuclearities stabilized by phosphines, pyridines, and N-heterocyclic carbene (NHC)-type ligands.⁷ Surprisingly, none of these copper hydrides contains both capping and interstitial hydrides.⁸ Some of them have been utilized in various catalytic reductions and hydrogenations.⁹

A series of air-stable Cu(I) clusters stabilized by dichalcogen donor ligands (L) as well as a hydride at their center have been successfully developed by our group in recent years.¹⁰ These clusters can be represented as [Cu₈HL₆]⁺, a tetracapped tetrahedral Cu framework, and [Cu₇HL₆], a tricapped tetrahedron; the hydride position in the latter was unequiv-

ocally proved by neutron diffraction. Encouraged by a recent report of a subnanometer-sized Cu cluster, Cu₈(C₇H₉N₂S)₄,¹¹ which is a part of topical research project on thiolate-passivated Au (Ag, Cu) nanoclusters¹² fabricated via wet-chemical borohydride reductions, we assumed that more of these nanosized Cu clusters stabilized by S-donor ligands could be generated if excess borohydrides were added into our original copper hydride cluster synthesis. Surprisingly, instead of the isolation of quantum-sized nanoclusters, a total of 11 hydrides were successfully incorporated into a Cu₂₀ cluster to give [Cu₂₀H₁₁(S₂P(OⁱPr)₂)₉] (**1_H**), the first elongated triangular orthobicupola array of 18 Cu atoms encapsulating a [Cu₂H₅]³⁻ ion. An elongated triangular orthobicupola framework, which is one of the 92 Johnson polyhedra¹³ and comprises of eight triangular faces and 12 quadrilateral faces in ideal D_{3h} symmetry, has not been realized in any elemental clusters prior to this study.¹⁴ In addition, the neutral copper hydrido complex [Cu₇H{S₂P(OⁱPr)₂}]₆ (**2_H**) was isolated. **1_H** and **2_H** are air- and moisture-stable solids, and we have also found that **1_H** can release H₂ gas under mild thermal conditions, upon irradiation with sunlight, and by reactions with acids at ambient temperature.

In a typical synthesis, **1_H** was prepared in 48% yield by the reaction of a mixture of NH₄[S₂P(OⁱPr)₂] and [LiBH₄·thf] with Cu(CH₃CN)₄PF₆ in tetrahydrofuran (THF). In addition, **2_H** was isolated in 10–15% yield. Compound **2_H** can also be synthesized in higher yield (73%) by the reaction of a Cu(I) salt, NH₄[S₂P(OⁱPr)₂], and [BH₄]⁻ in a 7:6:1 molar ratio. The chemical composition of **1_H** was first determined by positive-ion electrospray ionization mass spectrometry (ESI-MS), and its structure was established by single-crystal X-ray diffraction (XRD) (Figure 1). Figure 2 shows the most intense mass peak at *m/z* 3198.5 (calcd 3198.8), corresponding to the molecular weight of neutral **1_H**, whereas peaks in the lower and higher mass ranges could be attributed to the fragment [Cu₁₉H₉{S₂P(OⁱPr)₂}]⁺ (*m/z* 3132.6) and the adduct [Cu + Cu₂₀H₁₁{S₂P(OⁱPr)₂}]⁺ (*m/z* 3262.3), respectively. The theoretical isotopic pattern of **1_H** shows a great resemblance to the experimental one (Figure 2 inset). In the solid state, **1_H** is air- and moisture-stable. In solution, it is moderately stable at temperatures below 15 °C; in polar solvents (e.g., CH₂Cl₂, chloroform) it decomposes into **2_H** at room temperature after several weeks,

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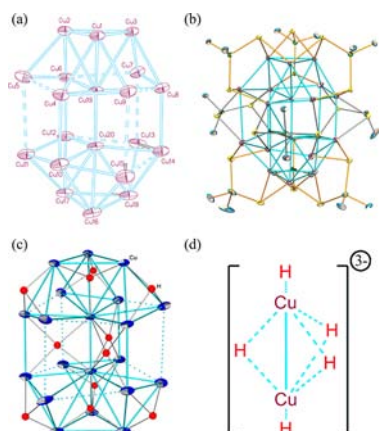


Figure 1. (a) An elongated triangular orthobicupola framework of 18 Cu atoms with solid and dashed (weak interaction) edges encapsulating a Cu_2 unit. Ellipsoids have been set at 50% probability. (b) A Cu_{20} cluster shielded by nine $[\text{S}_2\text{P}(\text{O}^i\text{Pr})_2]^-$ ligands. The isopropyl groups have been omitted for clarity. (c) Structure of the $\text{Cu}_{20}\text{H}_{11}$ moiety in $\mathbf{1}_\text{H}$. (d) Structure of the anchored $[\text{Cu}_2\text{H}_5]^{3-}$ unit. Color code: elongated triangular orthobicupola framework, cyan; Cu, purple; H, red; S, yellow; P, blue; O, green.

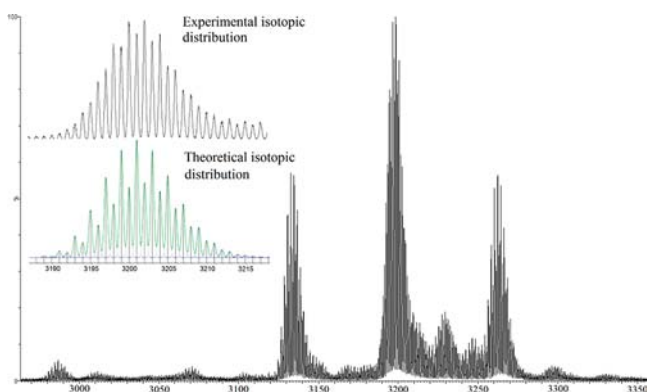


Figure 2. ESI mass spectrum of $\mathbf{1}_\text{H}$. The insets show the experimental and theoretical isotopic distributions.

but it is stable in nonpolar solvents (aromatic). Consistent with the XRD results (vide infra), the ^1H NMR spectrum of $\mathbf{1}_\text{H}$ shows two broad singlet hydride resonances at -0.99 and 2.80 ppm with an integration ratio of 6:3, but an expected resonance at ~ 1.4 ppm integrating for two more hydrides unfortunately overlapped with a broad doublet due to the methyl protons of the dithiophosphate (dtp) ligands. When the solvent was changed from CDCl_3 to toluene- d_8 , all of the hydride resonances were shifted downfield by ~ 0.5 ppm, and the resonance for the last two hydrides clearly appeared at 1.88 ppm (Figure S1A,C in the Supporting Information). The $-\text{OCH}-$ protons of the dtp ligands give rise to two resonances at 4.83 and 4.99 ppm with an integration ratio of 3:6, in line with the two chemical shifts identified in the ^{31}P NMR spectrum at 110.3 and 110.0 ppm, respectively. These data suggest the existence of two types of dtp ligands in the cluster. This assignment was confirmed by the ^1H NMR spectrum of the deuteride analogue $[\text{Cu}_{20}\text{D}_{11}(\text{S}_2\text{P}(\text{O}^i\text{Pr})_2)_9]$ ($\mathbf{1}_\text{D}$), which shows ligand resonances identical to those of $\mathbf{1}_\text{H}$ except for the lack of hydride resonances (Figure S1E). The ^2H NMR spectra of $\mathbf{1}_\text{D}$ in CHCl_3 {toluene} show three broad singlets at -0.89 { -0.48 }, 1.54 { 1.96 }, and 2.88 { 3.39 } ppm with an integration ratio of 6:2:3 (Figure S1B,D), strongly indicating that the 11

hydrides fall into three types in the title compound. These hydride shifts are significantly different from that of $\mathbf{2}_\text{H}$ (4.20 ppm), where the presence of the hydride was also confirmed by the resonance at 4.15 ppm in the ^2H NMR spectrum of $[\text{Cu}_7\text{D}\{\text{S}_2\text{P}(\text{O}^i\text{Pr})_2\}_6]$ ($\mathbf{2}_\text{D}$) (Figure S2A–C).

As shown in Figure 1, the polyhedral molecular structure of $\mathbf{1}_\text{H}$ consists of 20 Cu atoms, nine dtp ligands, and 11 hydrides. Even though the location of H atoms by XRD is difficult, the 11 hydrides in $\mathbf{1}_\text{H}$ could be approximately located from the Fourier difference map and refined freely. Whereas attempts to grow single crystals of suitable quality for neutron diffraction were unsuccessful, a density functional theory (DFT) geometry optimization¹⁵ of the model cluster $[\text{Cu}_{20}\text{H}_{11}(\text{S}_2\text{PH}_2)_9]$ was able to confirm the hydride positions determined by our low-temperature XRD study. Actually, the X-ray and DFT structures were in good agreement (see the relevant parameters in Table 1).

Table 1. Selected Structural Parameters and ^1H NMR Hydride Shifts for $\mathbf{1}_\text{H}$ and the Corresponding DFT-Computed Values

	bond lengths (Å)		^1H NMR shifts (ppm)		
	X-ray	DFT	exptl		
			CDCl_3	Tol- d_8	calcd
$\text{Cu}-\mu_3\text{-H}$	1.55(6)–1.81(8)	1.681–1.774	–0.99	–0.55	–1.03
$\text{Cu}-\mu_4\text{-H}_{\text{tet}}$	1.61(6)–1.83(6)	1.622–1.740	1.46	1.88	2.20
$\text{Cu}-\mu_4\text{-H}_{\text{square}}$	1.76(7)–1.88(7)	1.778–1.896	2.80	3.32	4.54
$\text{Cu}_{\text{outer}}-$	2.5284(9)–	2.536–	–	–	–
Cu_{outer}	2.7542(7)	2.773	–	–	–
$\text{Cu}_{\text{outer}}-$	2.6458(8)–	2.670–	–	–	–
Cu_{inner}	2.8595(7)	2.809	–	–	–
$\text{Cu}_{\text{inner}}-$	2.3079(7)	2.370	–	–	–
Cu_{inner}			–	–	–

The architecture of $\mathbf{1}_\text{H}$ reveals that an outer cluster of 18 Cu atoms forming an elongated triangular orthobicupola encapsulates an inner Cu_2 unit (Figure 1a). The skeleton of metal atoms can also be described as an elongated trigonal prism wrapped by a distorted hexagonal prism in which the two prisms share a common threefold axis. The 18 Cu atoms are further stabilized by nine dtp ligands, with each quadrilateral face of the two triangular cupola moieties and each alternative quadrilateral face of a distorted hexagonal prism capped by a dtp ligand in a tetrametallic tetraconnective (μ_2, μ_2) pattern (Figure 1b).¹⁶ The $\text{Cu}-\mu_2\text{-S}$ distances are in the range $2.2745(14)$ – $2.4404(13)$ Å. Additionally, each of the eight Cu_3 triangles, except the two situated on the C_3 axis, is further capped by a hydride ligand. The $\text{Cu}-\mu_3\text{-H}$ distances range from $1.55(6)$ to $1.81(8)$ Å. Astonishingly, an anchored $[\text{Cu}_2\text{H}_5]^{3-}$ unit is settled inside the elongated triangular orthobicupola in such a way that the two Cu atoms and two of the hydrides are located on the C_3 axis and the remaining three hydrides are located at the vertices of an equatorial triangle perpendicular to the C_3 axis. Hence, the five hydrides form a unique trigonal-bipyramidal arrangement around the central axial Cu_2 unit (Figure 1c,d). Whereas each of the two hydrides at the axial positions appears to reside in a tetrahedral cavity formed by one inner Cu atom and an outer Cu_3 triangle through which the C_3 axis passes, each of the three equatorial hydrides is located almost in the middle of a Cu_4 pseudosquare formed by the two

inner Cu atoms and two outer Cu atoms forming an edge the hexagonal prism. To the best of our knowledge, this represents the first four-coordinate hydride with a nearly square-planar geometry. Furthermore the simultaneous presence of six capping and five interstitial hydrides in \mathbf{I}_H is not only the first one in copper hydrides⁸ but also potentially provides an excellent model for hydrogen diffusion in metal lattices, such as the permeability of hydrogen in bulk Pd. The Cu– μ_4 -H_{tet} bond distance range, 1.61(6)–1.83(6) Å, encompasses the reported value of 1.73 Å for a four-coordinate hydride in binary CuH¹⁷ and is comparable with range of Cu– μ_4 -H_{square} bond lengths [1.76(7)–1.88(7) Å]. As a result, each inner Cu atom is tetrahedrally coordinated to four hydrides, and the outer Cu atoms display two kinds of coordination environment: six have trigonal S₂H coordination, and 12 have tetrahedral S₂H₂ coordination.

The central hexagonal prism of \mathbf{I}_H is distorted in such a way that each hexagon displays alternating Cu–Cu distances: three short [2.5277(8)–2.5570(8) Å] and three long [3.0445(9)–3.252(1) Å]. Therefore, the ideal D_{3h} symmetry of a regular elongated triangular orthobicupola is reduced to C_{3h} . All of the edge distances of each Cu₃ triangle are shorter than those of a Cu₄ quadrilateral, and the Cu–Cu distances associated with proximal hydrides are significantly shorter than those without hydrides in the neighborhood. The distance of 2.307(1) Å between the two inner Cu atoms approaches the shortest value reported for NHC-stabilized dinuclear copper hydrides.^{7,18} The average intraligand S···S bite distance is 3.43(5) Å.¹⁸

The cluster size of \mathbf{I}_H is similar to that of the recently reported phosphine-protected Au₂₀ cluster,¹⁹ which was also synthesized by borohydride reductions. Its structure reveals that the Au₂₀ core is generated from the fusion of two incomplete icosahedral Au₁₁ building units. The diameter of the spherical unit (C_{methyl}···C_{methyl}) in \mathbf{I}_H is ~17.8 Å, which is on the same order of magnitude as those of the smallest nanoparticles.²⁰ The solid-state structure of \mathbf{I}_H has a unique packing sequence of Cu atoms that can be viewed as an ABBA pattern normally identified in mixed metal oxide solids.²¹

Geometry optimization of the [Cu₂₀H₁₁(S₂PH₂)₉] model carried out at the BP86/Def2-TZVP level gave a structure very close to C_{3h} symmetry.¹⁵ Not only is this structure fully consistent with the experimental X-ray data, but the computed hydride NMR chemical shifts are in fairly good agreement with their experimental counterparts (Table 1).²² These results provide certainty about the hydride locations in \mathbf{I}_H . The natural orbital population analysis indicated that the hydrides of the encapsulated [Cu₂H₅]³⁻ unit have similar charges of –0.67, while the charge of the outer μ_3 -hydrides is smaller (–0.51), indicating that the latter are more covalently bonded, as confirmed by a comparison of the sums of the Cu–H Wiberg indices (WIs) (\sum Cu– μ_3 -H = 0.566; \sum Cu– μ_4 -H_{tet} = 0.361; \sum Cu– μ_4 -H_{square} = 0.372). Interestingly, the μ_4 -H_{tet} hydrides are bonded to the inner Cu atoms much more strongly than to the outer ones (WI = 0.199 and 0.054, respectively). Whereas the Cu_{inner}–Cu_{inner} separation is the shortest of all the Cu–Cu contacts, the corresponding WI (0.061) is among the lowest (WI range = 0.021–0.108). Although these values are only indicative at our level of calculation, they show that the Cu_{inner}–Cu_{inner} interaction is not different in nature from other Cu(I)–Cu(I) (i.e., d¹⁰–d¹⁰) interactions. This is in line with the fact that optimization of free [Cu₂H₅]³⁻ at the BP86/Def2-TZVP level leads to dissociation.

Any material targeted for hydrogen storage must not only be stable at room temperature but also require only a small amount of energy to release H₂ spontaneously.²³ To demonstrate the potential utility of as-synthesized \mathbf{I}_H , H₂ evolution experiments were performed under thermal, solar-energy, and acidic conditions. Preliminary variable-temperature ³¹P and ¹H NMR studies suggested that \mathbf{I}_H was converted into $\mathbf{2}_H$ accompanied by H₂ evolution (4.49 ppm) when the temperature was raised from 65 to 70 °C for 10 min (Figure S3A,B). The residual solution from thermolysis of \mathbf{I}_H also contained a phosphine byproduct of the dtp ligand, which appeared at 4.5 ppm in the ³¹P NMR spectrum. Under direct irradiation with sunlight, similar observations were also found within 3 h, and a lower H₂ evolution rate than for thermolysis was revealed. Furthermore, the evolution of H₂ was authenticated by analysis using a gas chromatograph equipped with a thermal conductivity detector. \mathbf{I}_H is capable of releasing 3.5 equiv of H₂ per molecule at temperatures above 65 °C (Figure S4A). Upon acidification with either a weak (acetic) or strong (hydrochloric) acid, \mathbf{I}_H can release 2.5 and 8 equiv of H₂ per molecule, respectively, at room temperature (Figure S4B,C). Hence, conversion of \mathbf{I}_H into $\mathbf{2}_H$ with concomitant H₂ evolution in a single-step process can be accomplished under mild thermal conditions, making \mathbf{I}_H a feasible system for the hydrogen industry as well as for catalysis of hydrogenation.

In summary, we have prepared and characterized an air- and moisture-stable nanospheric copper polyhydride whose structure is an elongated triangular orthobicupola array of 18 Cu atoms enclosing a [Cu₂H₅]³⁻ ion. The latter yields not only an unprecedented, Cu₂-centered trigonal-bipyramidal arrangement of five hydrides but also a hitherto unknown nearly square-planar geometry for each of the three equatorial hydrides. The salient feature of this new polyhydrido copper cluster in releasing H₂ gas under exceedingly mild conditions suggests its importance as a model for the design of new materials for hydrogen storage and hydrogenation catalysis.

■ ASSOCIATED CONTENT

📄 Supporting Information

Synthesis details, spectra, crystallographic data (CIF), computational studies, and complete ref 15 (as SI ref 3). This material is available free of charge via the Internet at <http://pubs.acs.org>. CCDC 922321 contains the supplementary crystallographic data for \mathbf{I}_H .

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Notes

The authors declare no competing financial interest.

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