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Polyhydrido Copper Clusters: Synthetic Advances, Structural Diversity, and Nanocluster-to-Nanoparticle Conversion

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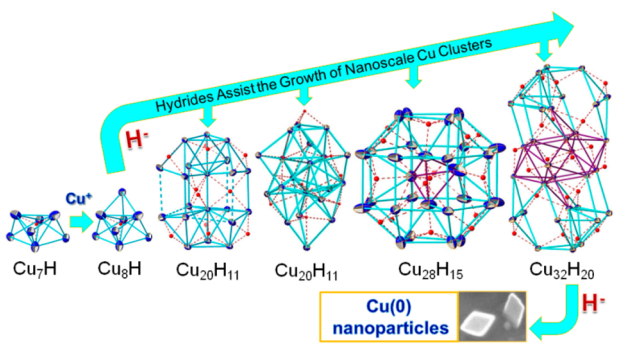
CONSPECTUS: Metal hydride clusters have historically been studied to unravel their aesthetically pleasing molecular structures and interesting properties, especially toward hydrogen related applications. Central to this work is the hydride ligand, H^-, the smallest closed-shell spherical anion known. Two new developments in polyhydrido nanocluster chemistry include the determination of heretofore unknown hydride coordination modes and novel structural constructs, and conversion from the molecular entities to rhombus-shaped copper nanoparticles (CuNPs). These advances, together with hydrogen evolution and catalysis, have provided both experimentalists and theorists with a rich scientific directive to further explore. The isolation of hexameric $[\{(Ph_3P)CuH\}_6]$ (Stryker reagent) could be regarded as the springboard for the recent emergence of polyhydrido copper cluster chemistry due to its utilization in a variety of organic chemical transformations. The stability of clusters of various nuclearity was improved through phosphine, pyridine, and carbene type ligands. Our focus lies with the isolation of novel copper (poly)hydride clusters using mostly the phosphor-1,1-dithiolato type ligands. We found such chalcogen-stabilized clusters to be exceptionally air and moisture stable over a wide range of nuclearities (Cu_7 to Cu_{32}). In this Account, we (i) report on state-of-the-art copper hydride cluster chemistry, especially with regards to the diverse and novel structural types generally, and newly discovered hydride coordination modes in particular, (ii) demonstrate the indispensable power of neutron diffraction for the unambiguous assignment and location of hydride ligand(s) within a cluster, and (iii) prove unique transformations that can occur not only between well characterized high nuclearity clusters, but also how such clusters can transform to uniquely shaped nanoparticles of several nanometers in diameter through copper hydride reduction.



The increase in the number of low- to high-nuclearity hydride clusters allows for different means by which they can be classified. We chose a classification based on the coordination mode of hydride ligand within the cluster. This includes copper clusters associated with bridging (μ_2-H) and capping (μ_3-H) hydride modes, followed by an interstitial (μ_4-H) hydride mode that was introduced for the first time into octa- and hepta-nuclear copper clusters stabilized by dichalcogen-type ligands. This breakthrough provided a means to explore higher nuclearity polyhydrido nanoclusters, which contain both capping (μ_3-H) and interstitial ($\mu_{(4-6)}$-H) hydrides. The presence of bidentate ligands having mixed S/P dative sites led to air- and moisture-stable copper hydride nanoclusters. The formation of rhombus-shaped nanoparticles (CuNPs) from copper polyhydrides in the presence of excess borohydrides suggests the presence of metal hydrides as intermediates during the formation of nanoparticles.

1. INTRODUCTION

Following more than a century of dormant activity, the last three decades have witnessed an upsurge of Group 11 metal (copper, silver, and gold) hydride research. This progress came about through advances in new synthetic precursors, more efficient means to elucidate structural aspects (notably by neutron diffraction), and more refined theoretical advances.

The first binary hydride for any metal was the copper hydride CuH, reported by Würtz in 1844 following the reduction of aqueous copper(II) sulfate with hypophosphorous acid,[1] and subsequently more efficient reducing agents.[2−4] The wurtzite-type structure of CuH was proved in 1926 by Muller and Bradley[5] and later confirmed by Goedkoop and Andersen with a neutron powder diffraction study.[6]

Recently, the binary CuH system has attracted interest due to the facile synthesis thereof through reductive sonication of an aqueous Cu^{2+} solution,[7] as well as the effect of temperature on its morphology.[8] Moreover, a novel hexagonal hydride phase, Cu_2H, which is chemically distinct from CuH, has been identified following high-pressure synthesis.[9] The formation of soluble LCuH species using phosphine and phosphite type ligands (L) proved very useful in advancing this chemistry.[10]

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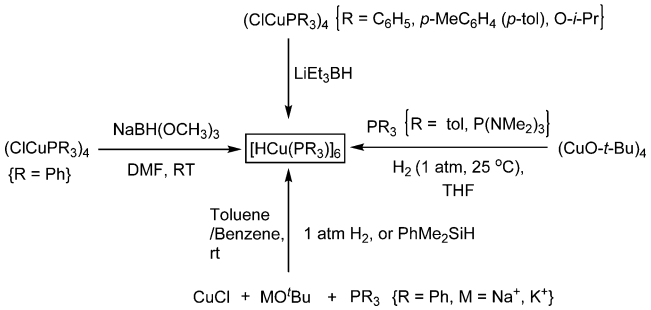
A major breakthrough was the isolation of the hexameric $[CuH(PPh_3)]_6$ cluster[11] in 1971, through modification by phosphine type ligands[12] and subsequently used extensively in organic reactions.[13] A series of air- and moisture-stable copper hydride clusters of the type $[Cu_8HL_6]^+$ and $[Cu_7HL_6]$ {L = dichalcogen (S or Se) donor ligand} with an interstitial (μ_4–H) hydride were unequivocally established by our group.[14−20] We subsequently explored polyhydrido copper clusters involving both capping and interstitial hydrides within a nanoscale metal framework with different coordination modes (μ_3, μ_4, μ_5, μ_6) in either a capping (bridged) or interstitial location,[21−25] with a few copper nanoclusters also developed by others.[26] The nanoclusters have various applications in areas such as hydrogen storage, but a fascinating new development is at the interface between molecular and materials chemistry with nanocluster conversion to rhombus-shaped CuNPs.

2. SYNTHESIS OF COPPER HYDRIDE CLUSTERS

A variety of hydride sources such as silanes, super hydride, H_2 gas, and borohydrides in the synthesis of copper hydride clusters have been applied; in addition, C–H activation of methanol[27a] and mono- or bidentate phosphine ligands (L) has been reported for mononuclear,[10,28] hydride bridged dimers of the type $[\{Cu_2(\mu\text{-}H)_2L_2\}]$,[29] $\{Cu_2(\mu\text{-}H)\}L_2]$,[30] trimer,[31] pentamer,[32] hexamer,[33] and octamer,[12a] of [LCuH] core clusters. Interestingly, the triangular $[Cu_2H]^+$ core bonding was described as a 3c-6e system. The metal cores in pentamer, hexamer, and octamer clusters adopt the distorted-trigonal-bipyramidal, distorted-octahedron, and dodecahedral frameworks, respectively. A hydrogenolysis (H_2, 1 atm) of the Cu–O bond in $(CuO\text{-}t\text{-}Bu)_4$ yielded a dimeric compound $[HCu(tripod)]_2$ in 75% yield.[34,35] By using different reagents, the hexameric $[HCu(PR_3)]_6$ cluster was isolated (Scheme 1).

Scheme 1. Preparation Methods for Hexameric $[HCu(PR_3)]_6$ Cluster

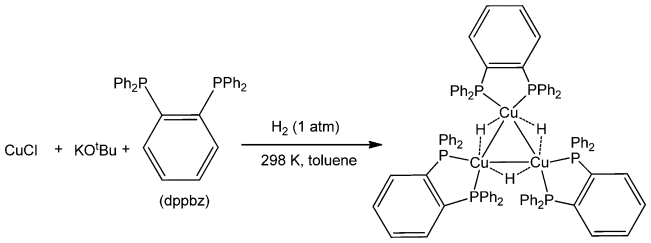


The yellow complex $[H_8Cu_8(dppp)_4]$ was isolated to observe the influence of a chelate effect in copper hydrides;[12a] the bidentate chelating ligand 1,2-bis(diphenylphosphino)benzene (dppbz) with molar equivalent CuCl and KO^{t}Bu, under an H_2 atmosphere (1 atm), yielded a 48-electron trimer $[(dppbz)\text{-}Cu(\mu_2\text{-}H]_3$ (Scheme 2).[31]

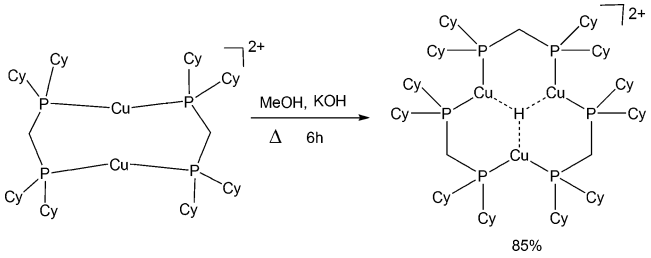
Che and co-workers demonstrated that a trinuclear copper hydride $[Cu_3(dcpm)_3(\mu_3\text{-}H)]^{2+}$ (dcpm = bis-(dicyclohexylphosphino)methane) could be prepared via C–H activation; see Scheme 3.[27a]

In contrast to tertiary phosphines, the N-heterocyclic carbene (NHC) ligands have a stronger interaction with the metal center, thereby minimizing ligand dissociation, and the dimeric $[(IPr)Cu(\mu\text{-}H)]_2$ complex was prepared in addition to

Scheme 2. Synthesis of Trimer $[(dppbz)\text{-}Cu(\mu_2\text{-}H]_3$



Scheme 3. Synthesis of Trinuclear Hydride Complex, $[Cu_3(dcpm)_3(\mu_3\text{-}H)]^{2+}$



$[(CAAC)CuH]_2$ in the presence of superhydride $LiHBEt_3H$ at −60 °C; see Scheme 4.[29a,b]

The dinuclear hydride $[(CAAC)CuH]_2$ is stable both in solution and solid-state at RT for a couple of weeks. A recent study revealed that with different reagents and conditions, the NHC (IPr) ligand supports the isolation of a colorless hydrido-bridged dicopper core cation $[((IPr)Cu)_2(\mu\text{-}H)]^+$ in a bent arrangement, Scheme 5.[30]

The scope of isolable copper polyhydrides changed dramatically when bidentate dichalcogen (E = S/Se) ligands and borohydrides were combined, summarized in Scheme 6A. By using the appropriate stoichiometric ratio of the reagents concerned following Scheme 6A, the relevant copper hydrides, $[Cu_{20}(H)_{11}\{S_2P(O^iPr\}_2)_9]$, $[Cu_{28}(H)_{15}(S_2CNR)_{12}]PF_6$, $[Cu_{32}(H)_{20}\{S_2P(O^iPr)_2\}_{12}]$, and $[Cu_{20}H_{11}\{Se_2P(O^iPr)_2\}_9]$, (NR = N^{n}Pr$_2$ or aza-15-crown-5) were isolated.[21−25] Similarly, by using bidentate phosphinothiolato S,P-type ligands, a copper polyhydride $[Cu_{18}H_7L_{10}I]$ (L = $S(C_6H_4)PPh_2$) has also been reported, Scheme 6B.[26a]

We have studied anion (F^-, Cl^-, Br^-, S^{2-}, Se^{2-}, etc.) recognition by Cu_8 clusters,[36] and introduced $[BH_4]^-$ as a hydride source to establish a series of interstitial hydride-containing octa- and heptanuclear copper clusters stabilized by dichalcogen (S, Se) donor ligands.[14−20,36] The monocationic tetracapped tetrahedral Cu^I_8 cluster converts into a neutral tricapped tetrahedral Cu^I_7 skeleton by removal of a capping Cu(I) atom through further reduction with 1 equiv of $[BH_4]^-$. The centered anions can all be replaced by hydride, but the reverse process has not yet been successful. The octa- and heptanuclear copper hydride clusters can also be obtained in good yields directly from a reaction mixture of [Cu^+ salt/dichalcogen ligand/BH_4^-] in a 8:6:1 and 7:6:1 ratios, respectively, Scheme 7. Interestingly, cationic Cu^I_8 clusters can be reformed by adding 1 equiv of Cu(I) salt to the neutral Cu^I_7 clusters and both clusters are stable toward air and moisture. Reactions of a linear tetraphosphine, with CuI and $NaBH_4$ afforded di- and tetranuclear copper hydride complexes, $[Cu_2(\mu\text{-}H)(\mu\text{-}dpmppm)_2]^+$ and $[Cu_4(\mu\text{-}H)_2\text{-}(\mu_4\text{-}H)(\mu\text{-}dpm\text{-}ppm)_2]^+$ (dpmppm = *meso*-bis[(diphenylphosphinomethyl)-phenylphosphino]methane).[26b] Expecting ligand substitution, a

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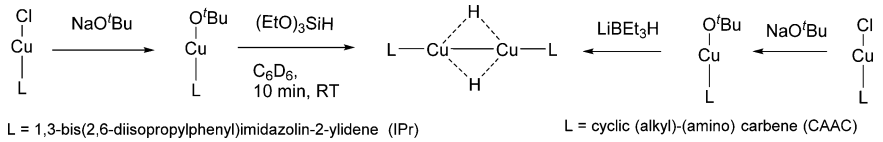
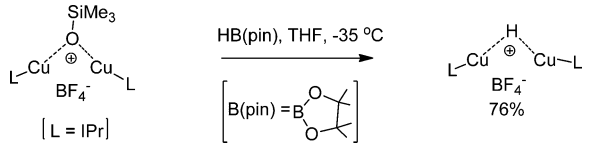
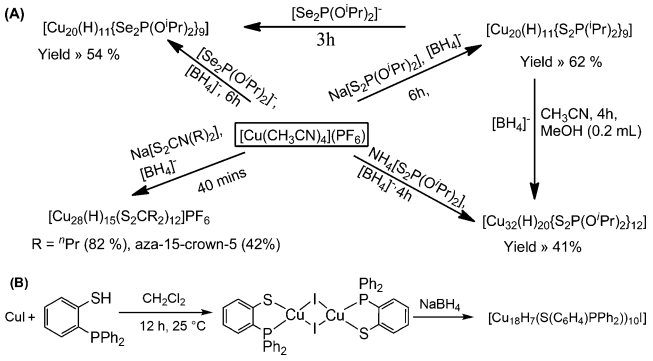
Scheme 4. Synthesis of Dinuclear Copper Hydrides



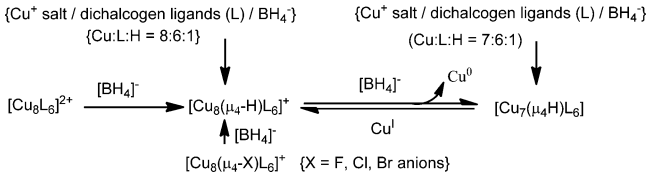
Scheme 5. Synthesis of Hydrido-Bridged Dicopper with Bent Cation



Scheme 6. Synthesis of Higher Nuclearity Copper Polyhydride Nanoclusters Using Dichalcogen (A) and Phosphinothiolate (B) Ligands



Scheme 7. General Synthesis Outline for $[Cu_8(\mu_4\text{-}H)L_6]^+$ and $[Cu_7(\mu_4\text{-}H)L_6]$ Clusters



reaction of 1,10-phenanthroline (phen) ligand with hexameric $[HCu(Ph_3P)]_6$ yielded $[Cu_{14}H_{12}(phen)_6(PPh_3)_4]^{2+}$.[26c] Recently, a related copper hydride cluster $[(Cp^*AlCu)_6H_4]$ ($Cp^* = C_5Me_5$) was formed by complete displacement of PPh_3 in $[HCu(Ph_3P)]_6$ via addition of $[(Cp^*Al)_4]$.[37]

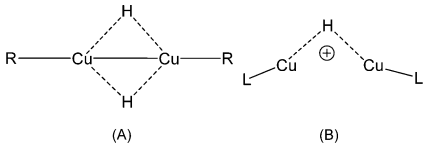
3. STRUCTURES OF COPPER HYDRIDES DETERMINED BY NEUTRON DIFFRACTION

Below we have targeted mainly structural descriptions of copper hydride clusters obtained by neutron diffraction while in the absence of such studies, we made brief mention of structures also obtained by X-ray diffraction.

3.1. μ_2-H, μ_3-H, and μ_6-H Systems

Hydride in the μ_2-H coordination mode has been observed from X-ray and other spectroscopic techniques in dinuclear copper complexes supported by NHC,[29a] CAAC,[29b] and 3-fold symmetric tridentate phosphine $MeC(CH_2PPh_3)_3$ ("tripod")[34] ligands, Chart 1A,B. The complex $[(\mu\text{-}H)_2Cu_2(\eta^2\text{-tripod})_2]$ was the first example of μ_2-H bridging two copper centers (Chart 1A).[34] The dimeric complex $[(IPr)Cu(\mu\text{-}H)]_2$ reveals very

Chart 1. μ_2-H Bridging Mode in Dinuclear Copper Complexes via X-ray Diffraction studies



R = [η^2-CH$_3$C(CH$_2$PPh$_2$)$_3$]; cyclic (alkyl)-(amino)carbenes: R, L = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-lidene)

short Cu−Cu (avg 2.30 Å) distances with a slight distortion from a linear C−Cu−Cu−C arrangement.[30] A density functional theory (DFT) study of triangular $[Cu_2H]^+$ core suggests that the $[((IPr)Cu)_2H]^+$ cation is an example of a bent and open three-center (3c-6e) interaction [Cu−H−Cu], where metals are held together through the bridging hydride (Chart 1B). A stabilized trinuclear complex with a chelating 1,2-bis(diphenylphosphino)benzene (dppbz) ligand is also associated with the μ_2-H mode.[31] The trimer $[(dppbz)\text{-}Cu(\mu_2\text{-}H]_3$ indicates that the hydride ligands are in a (μ_2)-bridging mode in the plane consisting of three Cu atoms with Cu−Cu distances at an average of 2.58 Å.

To date, μ_3-bridging hydrides were identified in tri-, penta-, hexa-, and octanuclear copper skeletons in the presence of mono- or bidentate phosphine ligands. However, μ_3-bridging hydride ligands in high-nuclearity copper (Cu ≥ 20) nanoclusters with dichalcogen or phosphinothiolate ligands have also been observed, vide infra. The hexamer $[HCu(PPh_3)]_6$ was the first example to reveal μ_3-bridging hydrides.[11] The cluster $[Cu_3(dcpm)_3(\mu_3\text{-}H)]^{2+}$ revealed a triangular copper plane along the various counteranions where hydride was located in the center of the Cu_3 core with Cu−H distances of ∼1.67 Å.[27] An oxo-bridged hydrolysis product, $[(Ph_3P)_6Cu_6H_4O]\cdot THF$, and a pentanuclear $[HCu(PPh_3)]_5$ cluster of a distorted-trigonal-bipyramidal metal array were reported using K-Selectride as a hydride source.[32] The octameric cluster $[H_8Cu_8(dppp)_4]$ revealed a dodecahedral form for the first time in a transition-metal homopolyatomic cluster.[12a] The Cu_8 skeleton revealed that the Cu−Cu distances [2.453(3)−2.517(3) Å and 2.676(3)−2.738(3) Å] caused a symmetry reduction from rigorous dodecahedral D_{2d} to S_4. The μ_6-H coordination mode of a hydride in the copper cluster $[Cu_6(\mu_6\text{-}H(\mu_3\text{-}Cl)(\mu_2\text{-}Cl)_3L_3]BF_4$ (L = trimethyltriazacyclohexane) was observed as a result of a C−H activation process.[27b] The copper(I) atoms are coordinated to a μ_6-H hydride ligand in the center of an octahedron at similar distances 1.85(3) Å.

Bau et al. reported a single-crystal neutron diffraction analysis of $[HCuP(p\text{-tolyl})_3]_6$, Figure 1.[33] It is consistent with previous studies showing copper atoms with six short [average 2.52 (3) Å] and six long [average 2.68 (4) Å] Cu−Cu edges in a distorted octahedron.

3.2. μ_4-H Systems

Generally, the presence of dichalcogen (S, Se) ligands L {L = dichalcogenophosph(in)ate, 1,1-dicyanoethylene-2,2-dithiolate (*i*-MNT), dithiocarbamates (dtc), and their selenium ana-

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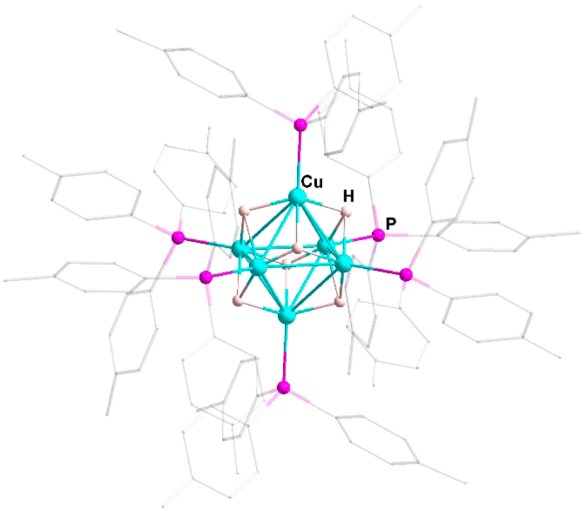

Figure 1. Neutron diffraction structure of $[HCuP(p\text{-tolyl})_3]_6$.

logues} assembles the Cu(I) atoms in a cubic arrangement with an empty site within the cluster center with a metal:ligand ratio of 8:6. Such clusters are capable of anion encapsulation at the center of the cube core.[36] For hydride anion encapsulation, the original cubic Cu^I_8 core transforming to a tetracapped tetrahedral framework was the first observed for any copper cluster.[15] The hydride ligand, which is spherical and the smallest closed-shell anion, was found to induce a tetrahedral contraction (in the empty cube) for four of the eight Cu atoms, resulting in a tetracapped tetrahedral geometry without altering the general bonding pattern (tetrametallic-tetraconnective; μ_2, μ_2) of the surrounding ligands and reducing the symmetry from T_h to T. Reported X-ray crystallographic studies of monocationic octanuclear copper clusters, for example, $[Cu_4(H)(\mu_3\text{-}Cu)_4\{S_2P(O^iPr)_2\}_6]^+$ shows that 8 copper atoms in 16 sites (each with 50% occupancy) to form two cubes with the one encapsulated by the other, Figure 2a.[14] Only four copper atoms per cube are fully occupied in a tetracapped tetrahedron (Figure 2b,c). A similar situation is also observed in the Cu^I_7 hydride clusters missing a capping Cu^I atom.

However, the X-ray diffraction study of $[Cu_8(H)\{S_2CNPr_2\}_6](PF_6)$[16] reveals that, unlike other reported hydrido copper clusters, none of the Cu atoms are disordered and the Cu^I_8 core is fully satisfied in a tetracapped tetrahedral geometry.

The cluster $[Cu_8(H)\{S_2CR\}_6](PF_6)$ was reacted with one equivalent of $[BH_4]^-$ and a neutral tricapped tetrahedral $[Cu_7(H)\{S_2CR\}_6]$ cluster was isolated. A single crystal neutron diffraction study of $[Cu_7(H)\{S_2CR\}_6]$ revealed a tricapped distorted tetrahedron copper framework in which the 4-coordinate hydride is shown to occupy the central site, (Figure 3a,b).[16] Neutron diffraction studies allowed for the unambiguous determination of H atom positions. The mean Cu−(μ_4-H) distance of 1.86(2) Å is slightly longer than the 1.76(3) Å (average), observed in a three coordinate hydride in $[(\mu_3\text{-}H)CuP(p\text{-tolyl})_3]_6$. Thus, the $[Cu_7(H)\{S_2CR\}_6]$ nuclearity followed $[(\mu_3\text{-}H)CuP(p\text{-tolyl})_3]_6$ in chronological order among copper hydride clusters studied by neutron diffraction.

3.3. Interstitial (μ_4-H, μ_5-H, and μ_6-H) with Capping (μ_3-H) Systems

Liu and co-workers reported the first copper hydrides containing both capping and interstitial hydrides within Cu_{20}[21,22,25] Cu_{28}[23] and Cu_{32}[24] nanosized frameworks. All the clusters were stabilized by dithiophosphate (or -carbamate) ligands. Intriguingly, the symmetric Cu_{20} cluster can be converted into a *chiral* Cu_{20} cluster by simple ligand exchange (S vs Se).[25] The clusters are stable in air and moisture at RT and suitably stable to grow X-ray and neutron quality single crystals.

Dithiocarbamate type ligands stabilized the first rhombicuboctahedral copper polyhydride complexes $[Cu_{28}(H)_{15}(S_2CNR)_{12}]PF_6$. The study by X-ray diffraction revealed that the metal hydride array contained two types of copper atom geometries namely an inner irregular tetrahedron and outer rhombicuboctahedral array [a 24 vertices Archimedean polyhedron]. The square faces (12_2) are capped by the 12 dithiocarbamate ligands in a tetrametallic tetraconnective (μ_2,μ_2) pattern with S···S bite distance of 3.059 Å (Figure 4a) and subtends the truncated octahedron of 24 sulfur atoms.

Neutron diffraction studies of this complex clearly revealed all 15 hydride positions of the $Cu_{28}H_{15}$ copper hydride core (Figure, 4b,c): (1) The eight triangular faces of the Cu_{24} rhombicuboctahedron are capped by eight 3-coordinate (μ_3-H) hydrides. Two different crystallographic sites define the positions of these eight hydrides: six hydrides are located in a general position, and two hydrides lie on the 3-fold rotation axis. (2) Two sets in a total of six truncated hydrides: four 5-coordinate (μ_5-H) hydrides and two (μ_6-H) hydrides that are coordinated to six copper atoms (4 Cu atoms of the square and

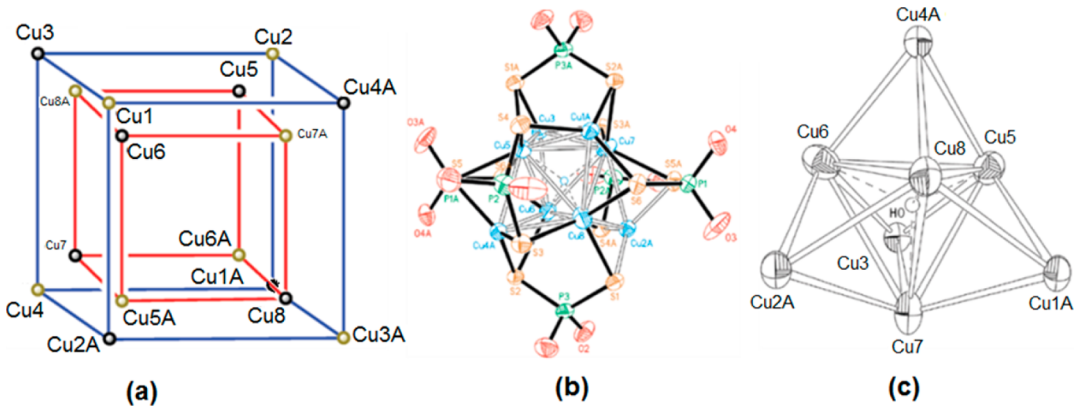

Figure 2. X-ray diffraction of $[Cu_8(H)\{S_2P(O^iPr)_2\}_6](PF_6)$ (a) 8 copper atoms in 16 sites, each with 50% occupancy, form two cubes with one inside the other. (b) Discrete structure. (c) $[Cu_8(\mu\text{-}H)]$ core.

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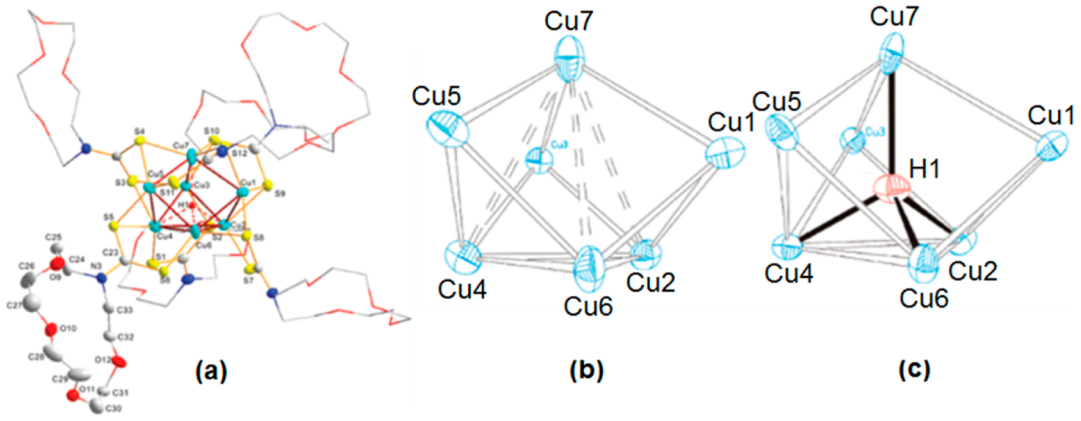

Figure 3. (a) Molecular structure of the $[Cu_4(\mu_4\text{-H})(\mu_3\text{-Cu})_3\{S_2C(\text{aza-15-crown-5})\}_6]$; H atoms omitted for clarity except the interstitial hydride. (b) Cu_7 framewrok displays an elongated tricapped pyramid from X-ray. (c) Cu_7H core drawing from neutron diffraction data.

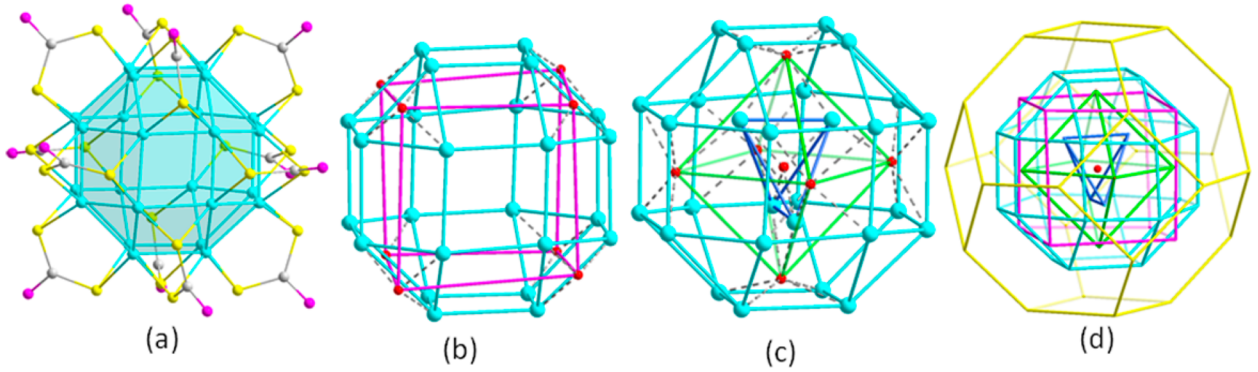

Figure 4. Structure of $[Cu_{28}(H)_{15}\{S_2CNPr_2\}_{12}]^+$. (a) Rhombicuboctahedral Cu_{24} core stabilized by 12 dtc ligand. (b) Eight (μ_3-H) capped triangular faces of Cu_{24}. (c) Truncated hydrides [4(μ_5-H) + 2(μ_6-H)] form octahedron motif and an interstitial hydride (μ_4-H) at center. (d) H@Cu_4(tetrahedron)@H_6(octahedron)@Cu_{24}(rhombicuboctahedron)@H_8(cube)@S_{24}(truncated octahedron). (Color code: Cu, cyan; S, yellow; H, red; C, gray; N, pink.)

2 Cu atoms of the inner tetrahedron) in trigonal prismatic geometry. (3) At the cluster center, one 4-coordinate (μ_4−H) hydride is present in a tetrahedral geometry. Whereas each inner copper atom is coordinated to three hydrides, each copper atom of the Cu_{24} shell has a distorted tetrahedral S_2H_2 coordination sphere. The simultaneous involvement of capping (μ_3-H), truncating (μ_5-H, μ_6-H), and interstitial hydrides (μ_4-H) were demonstrated within a metal cluster for the first time. The structure displays an intriguing geometric unit and can be expressed concentrically as H@Cu_4@H_6@Cu_{24}@H_8@S_{24}, revealing for each of the six separate chemical species, respectively, a center, tetrahedron, octahedron, rhombicuboctahedron, cube, and truncated octahedron (Figure 4d). The overall results generate a structure with appreciable aesthetic value that is hitherto unknown in cluster chemistry.

With the dithiophosphate (dtp) ligand, the cluster $[Cu_{20}(H)_{11}\{S_2P(O^iPr)_2\}_9]$ was isolated.[21,22] The X-ray structure revealed the first example of 18 Cu atoms in an elongated triangular orthobicupola (ETO) that encapsulates an inner Cu_2 unit with an exceptionally short Cu−Cu distance (2.307(1) Å) (Figure 5a). The ETO framework comprises 8 triangular faces and 12 quadrilateral faces in ideal D_{3h} symmetry. The ideal D_{3h} symmetry is reduced to C_{3h} due to a distorted central hexagonal prism caused by alternating Cu−Cu distances. The whole metal framework has been stabilized by 11 hydrides and nine dtp ligands (Figure 5a). A dtp ligand in a tetrametallic tetraconnective (μ_2,μ_2) pattern capped the two triangular

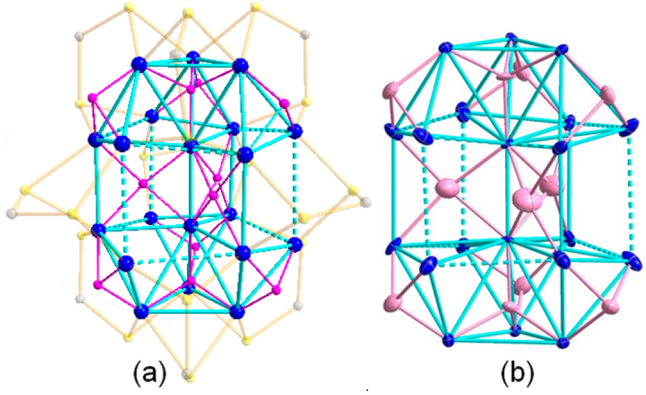

Figure 5. Structure of $[Cu_{20}(H)_{11}\{S_2P(O^iPr)_2\}_9]$. (a) X-ray structure and (b) neutron diffraction structure. (Color code: Cu, blue; Cu−Cu edges, cyan; S, yellow; P, gray; H, pink.)

cupola moieties (a quadrilateral face) and each alternative quadrilateral face of a distorted hexagonal prism, with average intraligand S···S bite distance of 3.43(5) Å. The diameter of the nanospherical unit (CH_3···CH_3) is ∼2 nm. The 11 hydrides display three different coordination modes to the Cu atoms (Figure 5b): six μ_3-H capped each of the Cu_3 triangles except the two situated on the C_3 axis, two μ_4-H in a tetrahedral cavity, and three μ_4-H in near square-planar geometry, which is unprecedented among metal hydrides. Inside the ETO, an

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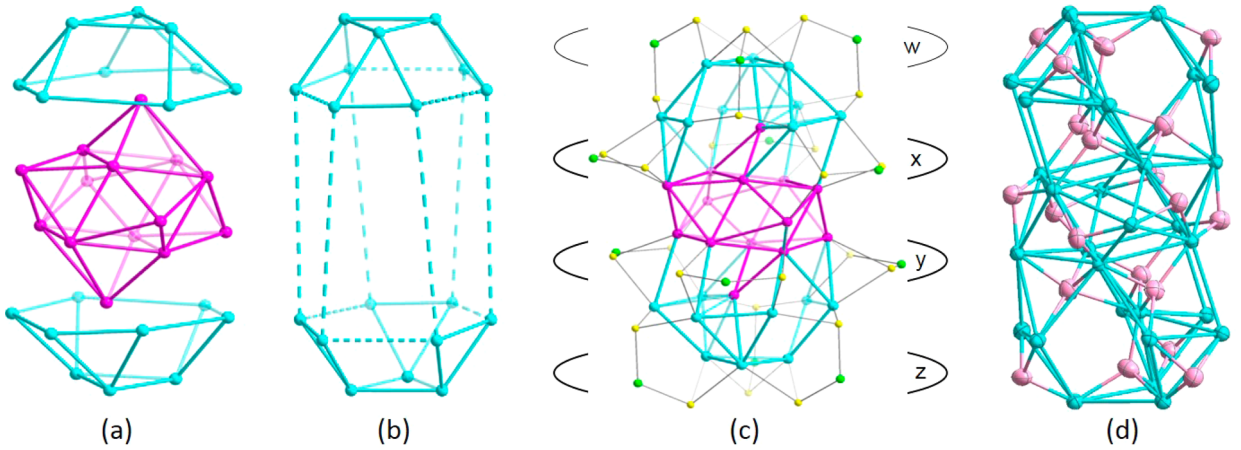

Figure 6. X-ray (a–c) and neutron (d) structure of $[Cu_{32}(H)_{20}\{S_2P(O^iPr)_2\}_{12}]$. (a) Hexacapped rhombohedron (pink) of 14 Cu atoms sandwiched between two triangular cupola (cyan) of (2 × 9) Cu atoms. (b) Elongated triangular gyrobicupola of Cu_{18} motif. (c) Twelve dtp ligands in four spherical rows (w, x, y, z) around metal core. (d) Position of 20 hydrides. (Color code: Cu, cyan and magenta; S, yellow; P, green; H, pink.)

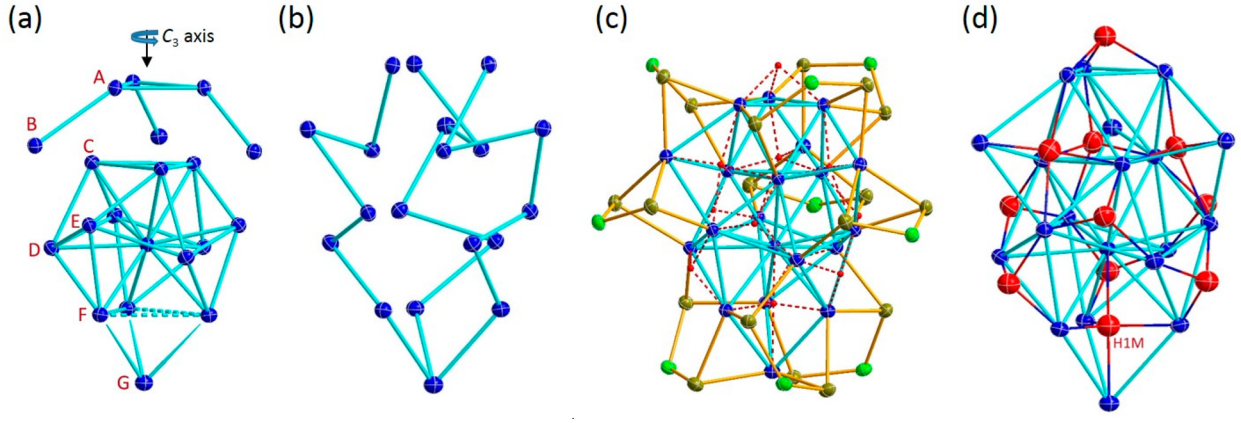

Figure 7. Structure of $[Cu_{20}(H)_{11}\{Se_2P(O^iPr)_2\}_9]$. (a) Intrinsic chiral Cu_{20} framework with different surface atom types (A–G). (b) Three anticlockwise copper strands within Cu_{20} core. (c) Cu_{20} core shielded by nine $[Se_2P(O^iPr)_2]^-$ ligands. (d) Five types of symmetry-related hydrides, determined by neutron diffraction. (Color code: Cu, blue; Cu–Cu edges, cyan; Se, yellow; P, green; H, red.)

anchored $[Cu_2H_5]^{3-}$ unit is embedded with two Cu atoms and two hydrides (μ_4-H_{tet}) located on the C_3 axis. The three remaining hydrides are located perpendicular (μ_4-H_{nsq}) to the C_3 axis. A unique trigonal bipyramidal arrangement was thus realized, formed by the five hydrides around the central axial Cu_2 unit.

In continuing our work on copper polyhydrides, we reported a $[Cu_{32}(H)_{20}\{S_2P(O^iPr)_2\}_{12}]$ nanocluster containing the highest number of hydrides in a molecular cluster.[24] It was the extended form of $[Cu_{20}(H)_{11}\{S_2P(O^iPr)_2\}_9]$ and reflects a structural correlation between the Cu_{20} and Cu_{32} skeleton and a logical extension of the synthesis methodology. The structure of Cu_{32} reveals a hexacapped distorted rhombohedral (R) core of 14 Cu atoms is sandwiched between two nest-like triangular cupola (C) fragments of (2 × 9) Cu atoms (Figure 6a). The 60° rotation of one of the cupolae of an ETO, as observed in Cu_{20}, yields an elongated triangular gyrobicupola polyhedron as found in Cu_{32}. A resemblance of one of the Catalan solids with idealized O_h symmetry is observed in the hexacapped rhombohedron that encompasses six (two interior, four exterior) capping Cu atoms on a rhombic cube. An elongated triangular gyrobicupola (Figure 6b), which is one of the 92 Johnson polyhedra and consists of 8 triangular faces and 12 quadrilateral faces in idealized D_{3d} symmetry, is generated by connecting the hexagonal bases of the two nest-like triangular cupolae fragments. Discovering both a Catalan and a Johnson solid within the same copper metal framework is rare but the Cu_{32} skeleton is one such example. Twelve dtp ligands in four spherical rows (w, x, y, z) and three ligands in each row stabilize the entire Cu_{32} cage (Figure 6c). Each dtp ligand has a tetrametallic, tetraconnective (η^4: μ_2, μ_2) pattern in rows (w, z), through capping of the quadrilateral face of a triangular cupola. Two dtp ligands in (η^4: μ_2, μ_2) and one dtp ligand in a trimetallic tetraconnective (η^3: μ_2, μ_2) pattern are in the two inner rows (x, y) through connection of each triangular cupola (hexagon Cu atoms) and hexacapped rhombohedron. The average dtp intraligand S···S bite distance is 3.42(3) Å, which is comparable to the Cu_{20} (avg. 3.43(5) Å) system. The bare copper atom cage has a diameter of approximately 11.4 Å and extends to 20.9 Å with inclusion of the ligand sphere.

The positions of 20 hydrides of the $Cu_{32}H_{20}$ core are clearly shown by neutron diffraction studies performed with the TOPAZ instrument of the ORNL Spallation Neutron Source. Based on their coordination modes, they can be grouped into 12 μ_3-H (6 + 6), 6 μ_4-H (2 + 4), and 2 μ_5-H ligands (Figure 6d). Six μ_3-H ligands cap six of the eight Cu_3 triangles (the two apical triangles remain uncapped) as found in Cu_{20}. In the hexacapped rhombohedron, the other six μ_3-H ligands bridge

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the Cu_3 triangles. At the center of one cupola are two μ_4-H ligands that lie in a tetrahedral cavity formed by one capping Cu atom of the hexacapped rhombohedron and an apical Cu_3 triangle. The two interfaces formed between the cupolae and hexacapped rhombohedron is the location of the remaining four μ_4-H and two μ_5-H ligands. Four Cu atoms related to one cupola Cu atom and the two adjacent triangular faces of hexacapped rhombohedron define the coordination of the approximate square pyramidal μ_5-H ligand. Tri-, tetra-, and pentacoordinated hydrides (in interstitial and capping modes) are revealed in this Cu_{32} cluster for the first time. Unsymmetrical bonding is evident from the Cu-μ_5-H bond lengths that are in the range of 1.774(9)−2.121(8) Å.

The first example of polyhydrido copper nanoclusters $[Cu_{20}(H)_{11}\{Se_2P(O^iPr)_2\}_9]$,[25] which displays an intrinsic chiral inorganic core of C_3 symmetry, was synthesized from an achiral $[Cu_{20}(H)_{11}\{S_2P(O^iPr)_2\}_9]$ cluster of C_{3h} symmetry via a ligand metathesis (Scheme 6A). The metal framework can be best described as a distorted centered-cuboctahedral Cu_{13} core of which two triangular faces along the C_3 axis are capped by a Cu_6 cupola and a single copper atom, respectively (Figure 7a). Classifying the 19 surface Cu atoms into seven types of symmetry-related atoms (labeled A-G) in a ratio of 3:3:3:3:3:3:1 (Figure 7a) reveal the first structural evidence for any nanoscale hydrido metal cluster bearing an intrinsic chiral metallic core with three anticlockwise copper strands (Figure 7b). The whole copper framework is covered by nine diselenophosphate ligands with equal distribution in three spherical rows either in a tetrametallic tetraconnective (η^4:μ_2, μ_2) or trimetallic tetraconnective (η^3:μ_2, μ_2) pattern (Figure 7c). The neutron diffraction study shows the 11 hydrides (grouped into five types of symmetry-related atoms) of which seven (1 + 3 + 3) are capping μ_3-H ligands and four (3 + 1) are in interstitial μ_5-H locations (Figure 7d).

One of the five-coordinated interstitial hydrides (μ_5-H1M) is located on the C_3 axis in trigonal bipyramid, which represents the first example of a five-coordinated hydride in trigonal bipyramidal geometry in any copper hydrides. Overall, two structurally characterized dichalcogen-stabilized polyhydrido copper(I) clusters that differ only by the nature of the chalcogen, have distinct molecular structures and metal cores, and therefore provide an example of pseudoisomers.

The Van Leeuwen group isolated an air- and moisture stable $[Cu_{18}H_7L_{10}I]$ nanocluster with the 2-(diphenylphosphino)-benzenethiol ligand (L = $[SC_6H_4PPh_2]^-$).[26a] The framework of 18 copper atoms can be described as a central core of 8 Cu atoms formed by two butterfly structures (4 Cu atoms each; Figure 8a). The remaining 10 Cu atoms surrounding the internal Cu core are connected to S and P atoms (Figure 8b). DFT study suggests the presence of 5(μ_3-H) and 2(μ_2-H) bonding.

Hayton and co-workers reported the $[Cu_{14}H_{12}(phen)_6(PPh_3)_4]^{2+}$ cluster which features a tetrahedral $[Cu_4]^{4+}$ core connected through Cu−Cu interactions, and encapsulated into a diamondoid arrangement of 10 Cu^I centers (Figure 9).[26c] These 10 copper centers are coordinated to 4 PPh_3 (tetrahedron) and 6 phen (octahedron) ligands. Overall, this complex features four hexagonal faces, wherein each face is situated opposite a PPh_3 ligand. The metrical parameters of the tetrahedral $[Cu_4]^{4+}$ core (avg Cu_{tet}−Cu_{tet} = 2.893 Å) are nearly identical to those of the $[Cu_4(\mu_4\text{-H})]^{3+}$ core in $[Cu_8H\{S_2CN^nPr_2\}_6]^+$ (2.894(2)−2.989(2) Å). DFT studies revealed that 12 hydrides were coordinated to the hexagonal Cu faces, in four of three groups in a μ_3-H fashion. ^{1}H and ^{2}H NMR of hydride and deuteride containing Cu_{14} shows peaks at 3.45 and 3.58 ppm and assign all 12H in an identical environment.

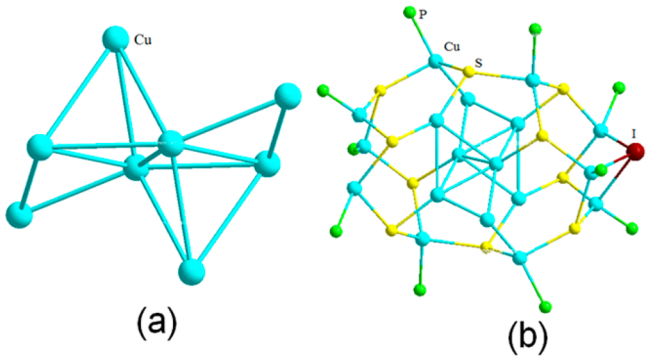

Figure 8. Structure of $[Cu_{18}H_7L_{10}I]$. (a) Two butterfly structures of 8 Cu atoms. (b) Skeleton of nanocluster formed by 18 Cu, 10 S, I, and 10 P atoms.

4. CLUSTER PROPERTIES AND APPLICATIONS

We have embarked on preliminary studies on hydrogen storage and H_2 evolution on the Cu_{20} and Cu_{28} clusters under various conditions. The hydride-centered dithiophosphate cluster $[Cu_8(\mu_4\text{−H})\{S_2P(OEt)_2\}_6](PF_6)$ was applied as a new catalyst to the 1,3-dipolar cycloaddition of organic azides and alkynes for preparing substituted trizoles.[38] Preliminary results look encouraging, but are still a work in progress and thus do not form part of this Account.[21]

4.1. Nanocluster-to-Nanoparticles Conversion

Studies were performed on the formation of Cu nanoparticles from the higher nuclearity copper polyhydrido clusters. For example, Cu_{32} clusters in the presence of excess $NaBH_4$ (20-fold) nucleated into nanometer-sized copper particles.[24] SEM images and the EDS spectrum of the resulting particles are depicted in Figure 10A and B, and show unique rhombus-shaped copper nanoparticles having a mean edge length of 92 ± 4 nm. Figure 10C shows an XRD pattern with diffraction peaks at 2θ = 43.3, 50.4, and 74.1 that can be indexed as the [111], [200], and [220] planes, respectively, of face-centered cubic copper. The formation of copper nanoparticles from the corresponding copper polyhydrides strongly suggests that the formation of metal hydride nanoclusters could occur prior to its collapse into nanoparticles driven by chemical reduction using excess $[BH_4]^-$.

4.2. H_2 Evolution and Catalytic Activities

The isolated copper polyhydrides evolved H_2 under extremely mild conditions at 60 °C, weak acidifications and most importantly under solar energy. The H_2 evolution was first studied on the Cu_{20} cluster and later proceeded to Cu_{28} with a reproducible cycle of H_2 generation as shown in Figure 11.[21,23] Recently, Sadighi et al. reported a dicopper hydride complex $[Cu_2(\mu\text{-H})(IPr)_2]^+$, which reacts with CO_2 under mild conditions to afford a formate-bridged dicopper complex via the mononuclear complex [Cu-(HCOO) (IPr)].[30] The formate-generating process is a crucial step in the initial stage of CO_2 hydrogenations.[39] The reactivity with unsaturated terminal alkynes and methanol are also described.[30,27a] The recently isolated complex $[Cu_2(\mu\text{-H})(\mu\text{-dpmppm})_2]^+$ showed facile CO_2 (1 atm) insertion at room temperature, leading to a formate-bridged dicopper complex $[Cu_2(\mu\text{-HCOO})$

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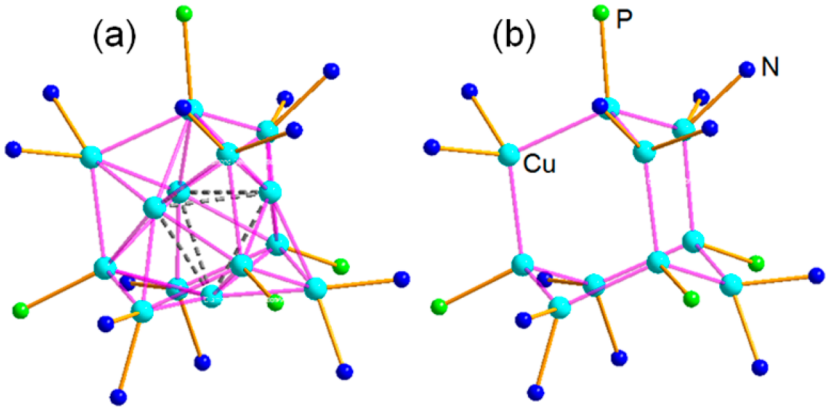

Figure 9. (a) $[Cu_4]^{4+}$ core with diamondoid Cu_{10}. (b) Outer Cu shell, reminiscent of adamantane structure in $[Cu_{14}H_{12}(phen)_6(PPh_3)_4]^{2+}$ while removing of $[Cu_4]^{4+}$ core.

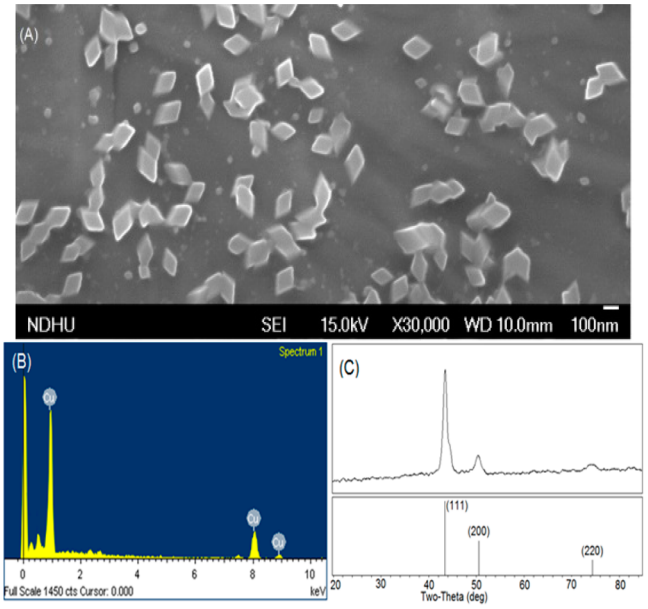

Figure 10. Analysis of Cu nanoparticles obtained from Cu_{32}. (A) SEM image. (B) EDS spectrum. (C) Powder XRD patterns (top), standard data for Cu metal, JCPDS No. 04-0836 (bottom).

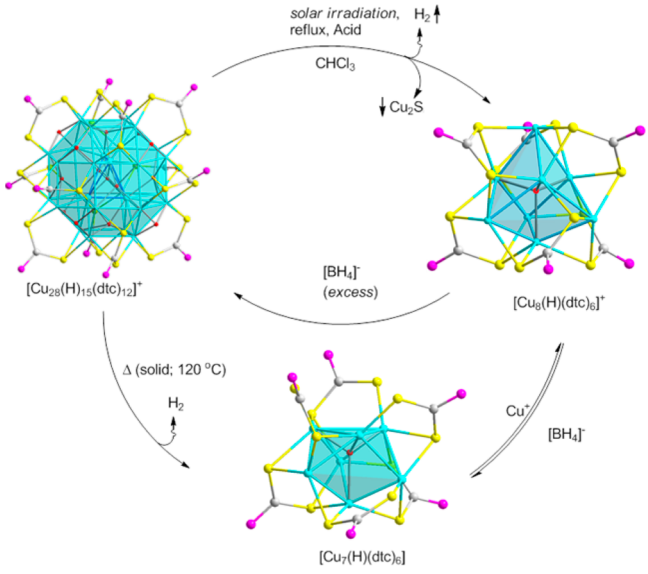

Figure 11. Reproducible cycle for H_2 evolution under various conditions.

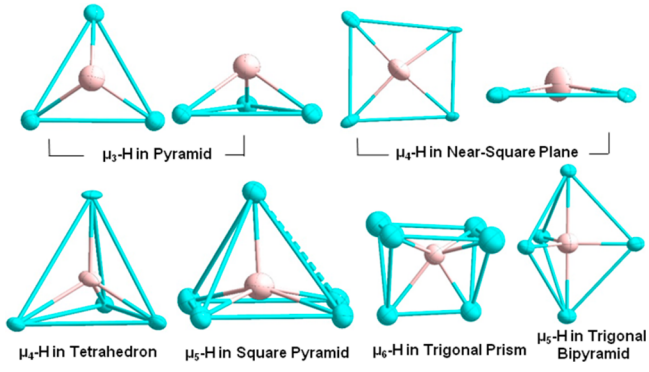

Figure 12. Summary of different coordination modes for hydride in copper hydride clusters as described in this Account.

$(dpmppm)_2]^+$.[26b] Along with the wide ranging applications in organic reactions,[13] the hexameric cluster $[HCuPPh_3]_6$ also gives the formate $(Ph_3P)_2CuOCOH$ on treatment with CO_2.[40]

5. SUMMARY AND FUTURE PERSPECTIVES

Despite the satisfactory progress on copper polyhydrides made by our group with neutron diffraction studies during the past decade, detailed molecular studies on discrete copper hydride complexes has previously been limited to only the hexanuclear cluster $[HCuP(p\text{-tolyl})_3]_6$. We expanded this research significantly with bidentate dithiolate ligands for the stabilization of copper polyhydride nanoclusters with variable nuclearities ranging from Cu_7, Cu_{20}, Cu_{28}, and Cu_{32}, and unambiguously confirmed the locations of hydrides in different coordination modes by neutron diffraction, as summarized in Figure 12, along with other spectroscopic techniques. These polyhydrido clusters reveal aesthetically pleasing molecular structures with the presence of interstitial as well as capping hydrides along with different types of coordination modes.

The sequential conversion of Cu_{20} into Cu_{32} and then into CuNPs in the presence of $[BH_4]^-$ indicates the potential to discover yet unknown metal hydrides, which could be intermediates prior to the formation of metal nanoparticles under wet chemical reductions methods. This could establish a framework to develop a bridge between copper hydride chemistry and nanosized materials chemistry.

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Notes

The authors declare no competing financial interest.

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