Inorganic Chemistry
Article
pubs.acs.org/IC

Neutron Diffraction Studies of a Four-Coordinated Hydride in Near Square-Planar Geometry

Jian-Hong Liao,[†] Rajendra Singh Dhayal,[†] Xiaoping Wang,[‡] Samia Kahlal,[§] Jean-Yves Saillard,[§] and C. W. Liu*[,†]

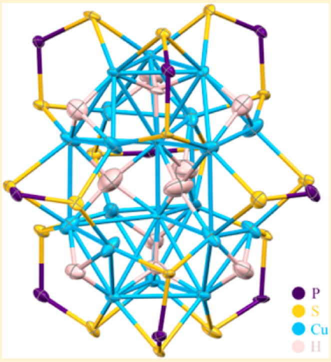
[†]Department of Chemistry, National Dong Hwa University, Hualien 97401, Taiwan, R.O.C.

[‡]Chemical and Engineering Materials Division, Neutron Science Directorate, Oak Ridge National Laboratory, Oak Ridge 37831, United States

[§]Institut des Sciences Chimiques de Rennes, UMR 6226 CNRS-Université de Rennes 1-Ecole Nationale Supérieure de Chimie de Rennes, Avenue du Général Leclerc, 35042 Rennes, France

Ⓢ *Supporting Information*

ABSTRACT: The structure of a nanospheric polyhydrido copper cluster, $[Cu_{20}(H)_{11}\{S_2P(O^iPr)_2\}_9]$, was determined by single-crystal neutron diffraction. The Cu_{20} cluster consists of an elongated triangular orthobicupola constructed from 18 Cu atoms that encapsulate a $[Cu_2H_5]^{3-}$ ion with an exceptionally short Cu−Cu distance. The 11 hydrides in the cluster display three different coordination modes to the Cu atoms: six μ_3-hydrides in a pyramidal geometry, two μ_4-hydrides in a tetrahedral cavity, and three μ_4-hydrides in an unprecedented near square-planar geometry. The neutron data set was collected for 7 days on a small crystal with dimensions of 0.20 mm × 0.50 mm × 0.65 mm using the Spallation Neutron Source TOPAZ single-crystal time-of-flight Laue diffractometer at Oak Ridge National Laboratory. The final *R*-factor was 8.63% for 16,014 reflections.



■ INTRODUCTION

Metal hydride complexes continue to attract broad attention because of their fascinating structural and bonding characteristics[1,2] and their roles as key intermediates in various heterogeneous and homogeneous catalysts.[3] Recent practical applications of metal hydrides include their contributions to hydrogen storage technology.[4] Thus, understanding the precise coordination geometry of hydride compounds will undoubtedly help the scientific community develop better hydrogenation catalysts and hydrogen storage materials.

Since the development of neutron diffraction, a diverse array of metal hydride complexes have been characterized to emphasize the rich variety of metal−hydride interactions.[5] Neutron diffraction is the method of choice for detecting hydrogen atoms, especially for systems that contain heavy metals. Unlike the scattering factors of X-rays, those of neutrons are not proportional to the atomic number. For example, the scattering length for H is −3.739 fm, which markedly differs from the analogous value for Cu (i.e., 7.718 fm).[6] This feature makes neutron diffraction an ideal technique for studying metal hydride complexes.

In addition to the terminally coordinated mode, several bridging types of hydride ligands have been characterized by single-crystal neutron diffraction.[7] In 1981, Bau and co-workers reported that $[HCo_6(CO)_{15}]^-$ has a six-coordinated hydride in an octahedral cavity,[7c] and in 1997, the same group reported that $[H_2Rh_{13}(CO)_{24}]^{3-}$ has a five-coordinated hydride in a square-pyramidal cavity.[7e] Furthermore, a five-coordinated hydride in a trigonal bipyramidal geometry appears to exist in the heterometallic cluster compound $[\{(Cp'Y)_4(\mu\text{-}H)_6\}(\mu\text{-}H)_5WCp^*]$.[8k] Hou and co-workers developed a series of lanthanide polyhydrido complexes,[8] including $[(C_5Me_4SiMe_3)YH_2]_4(THF)$,[8f] which consists of one four-coordinate hydride in a tetrahedral geometry, one face-sharing 3-coordinate hydride in a pyramidal geometry, and six edge-bridging 2-coordinate hydride ligands. To date, however, a four-coordinate hydride in a square-planar geometry has never been characterized by single-crystal neutron diffraction.

Since 2009, our research group has reported a series of tetracapped tetrahedral copper clusters encapsulating a four-coordinate hydride at the cluster center.[9] Further reaction of hydride-centered octanuclear copper clusters with borohydride yields the tricapped tetrahedral copper cluster,[10] whose central four-coordinated hydride was established by a neutron diffraction study of the compound $[Cu_7(H)\{S_2C(aza\text{-}15\text{-}crown\text{-}5)\}_6]$.[10a] Subsequently, we discovered that an added hydride source can assist the growth of copper-cluster nuclearity. Thus, two aesthetically pleasing, air-stable nanospheric copper polyhydrides were characterized. One of these copper polyhydrides characterized by neutron diffraction is the recently communicated "Chinese puzzle molecule",

Received: July 21, 2014
Published: October 7, 2014

dx.doi.org/10.1021/ic501747e | *Inorg. Chem.* 2014, 53, 11140−11145

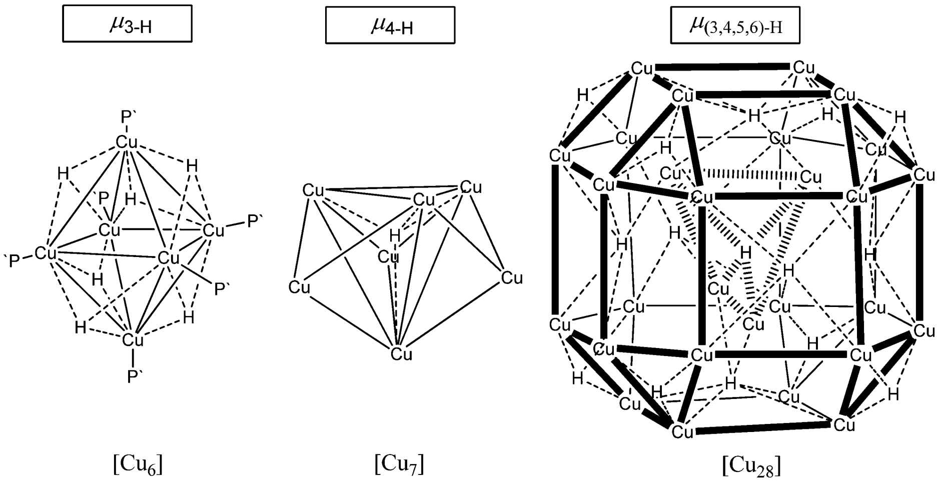


Figure 1. Neutron diffraction studied copper hydride clusters and various coordination modes of hydrides within Cu_6, Cu_7, and Cu_{28} cores. P′ = P(*p*-tolyl)$_3$. Both Cu_7 and Cu_{28} cores are stabilized by dithiocarbamate ligands, which are not shown for clarity.

$[Cu_{28}(H)_{15}\{S_2CN(^nPr)_2\}_{12}](PF_6)$,[11] which contains one central interstitial hydride (μ_4-H) in a tetrahedral geometry, eight outer-triangular-face-capping hydrides (μ_3-H), and six square face-truncating hydrides $[2(\mu_6\text{-H})+4(\mu_5\text{-H})]$ to form an unprecedented bridge between the inner tetrahedral and outer rhombicuboctahedral copper atom arrays (Figure 1). The other copper polyhydride is $[Cu_{20}(H)_{11}\{S_2P(O^iPr)_2\}_9]$, which is the first example of an elongated triangular orthobicupola copper atom array of C_{3h} symmetry.[12] This cluster was characterized by X-ray diffraction, multinuclear NMR spectroscopy, electrospray ionization (ESI) mass spectroscopy, and DFT calculations. Both the X-ray diffraction results and the DFT calculations suggested that 11 hydrides exhibit three different types of coordination environments: μ_3-H in a pyramidal geometry, μ_4-H in a tetrahedral cavity, and μ_4-H in a near square-planar geometry. Because both μ_3-H in a pyramidal geometry[13b] and μ_4-H in a tetrahedral geometry have been characterized by neutron diffraction in copper(I) hydride clusters (Figure 1), a μ_4-H in a square-planar geometry remains unknown among the characterized metal hydrides. Thus, the characterization of the square planarity revealed in three (i.e., μ_4-H) of the 11 hydrides of the Cu_{20} cluster using the same technique will be of urgent interest. For this reason, we performed a neutron diffraction study and herein report the high-resolution, single-crystal neutron diffraction results for $[Cu_{20}(H)_{11}\{S_2P(O^iPr)_2\}_9]$, which unequivocally authenticate a four-coordinated hydride in near square-planar geometry.

■ RESULTS AND DISCUSSION

$[Cu_{20}(H)_{11}\{S_2P(O^iPr)_2\}_9]$ was prepared using a previously reported synthetic method;[12] details of the synthesis and crystal preparation are provided in the Experimental Section. A yellow crystal with dimensions of 0.20 mm × 0.50 mm × 0.65 mm (0.065 mm^3) was placed on a single-crystal diffractometer. This crystal size is relatively small for a general neutron diffraction experiment. The data were collected at 100 K for 7 days. A total of 274 atoms in the asymmetric unit were determined in the triclinic cell and were refined anisotropically (except the disordered groups), which resulted in up to 1966 parameters. The final *R*-factors converged to $R1 = 0.0863$ and $wR2 = 0.1835$ for 16,014 reflections with $I > 3\sigma(I)$. The neutron crystallographic data are listed in Table 1.

Table 1. Neutron Crystallographic Data of $[Cu_{20}H_{11}\{S_2P(O^iPr)_2\}_9]\cdot 1.5(\text{benzene})$

formula	$C_{54}H_{137}Cu_{20}O_{18}P_9S_{18}\cdot 1.5C_6H_6$
formula weight	3318.72
crystal system	Triclinic
space group	*P*(−)1
a (Å)	16.2820(4)
b (Å)	16.6588(4)
c (Å)	24.1228(6)
α (deg)	86.409(1)
β (deg)	87.479(1)
γ (deg)	65.658(2)
V (Å^3)	5948.5(3)
Z	2
T (K)	100(2)
λ (Å)	0.4−3.5
ρ (Mg m^{-3})	1.853
μ (mm^{-1})	$0.1218 + 0.1717\lambda$
measured reflns ($I > 3\sigma I$)/unique	16014/16014
no. of params refined/restraints	1966/151
$R1^a$(observed), $wR2^b$(all)	0.0863, 0.1835
GOF	1.219
residual nuclear density (fm Å^{-3})	1.622 and −0.908

$^a R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $^b wR2 = \sum[w(F_o^2 - F_c^2)_2]/\sum[w(F_o^2)^2]$.

The neutron diffraction analysis of $[Cu_{20}(H)_{11}\{S_2P(O^iPr)_2\}_9]$ revealed that the Cu_2-centered elongated triangular orthobicupola structure consists of 20 Cu atoms, 11 hydrides, and nine dithiophosphate (dtp) ligands (Figure 2a). The precise locations of the 11 hydrides, whose positions are similar to those identified from X-ray data and DFT calculations, were determined. The hydrides exhibit three different types of coordination environments in this Cu_{20} cluster: six μ_3-H are each capped on the triangular face, two μ_4-H are in tetrahedral cavities, and three μ_4-H are in a near square-planar geometry (Figure 2b). Whereas a C_3 rotational axis passes simultaneously through the two uncapped triangular faces, the tetrahedral hydrides, and the two inner Cu atoms (Figure 2b), a σ_h horizontal plane contains three near square-planar hydride atoms. Thus, according to the neutron data, the Cu_{20} cluster possesses C_{3h} symmetry. Notably, the hydride locations in a series of dichalcogen-passivated copper hydride complexes

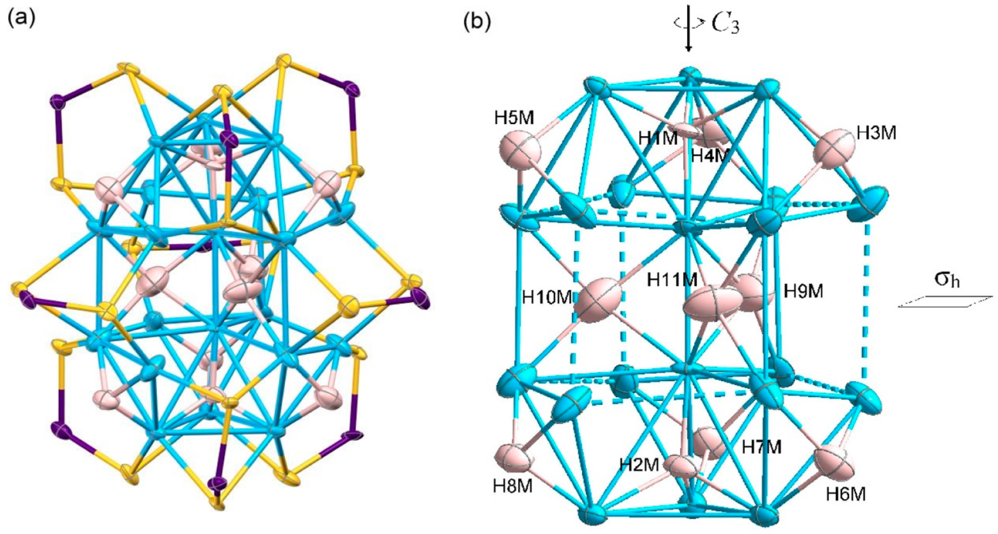


Figure 2. Single-crystal neutron diffraction: (a) the structure of $[\mathrm{Cu_{20}(H)_{11}\{S_2P(O^iPr)_2\}_9}]$ with the isopropoxy groups omitted for clarity (thermal ellipsoids are drawn with 50% probability) and (b) the structure of the $\mathrm{Cu_{20}H_{11}}$ core. Pink, H; cyan, Cu; purple, P; yellow, S.

determined using complementary X-ray and ^{1}H NMR data in conjunction with DFT calculations are highly consistent with the structural results obtained from neutron diffraction. The small systematic differences observed between the neutron and DFT geometrical data are attributed to the simplification of the computed molecular model and the exclusion of crystal packing forces in the calculations. Table 2 lists the copper hydride distances determined from both the experimental neutron data and the DFT calculations performed on the $[\mathrm{Cu_{20}(H)_{11}(S_2PH_2)_9}]$ model.

The Cu−(face-capping μ_3-H) distances are in the range of 1.65(1) Å−1.77(1) Å (avg 1.71(4) Å). These distances are similar to the bond lengths reported for the Cu−(μ_3-H) moieties in $[\mathrm{HCu\{P(\mathit{p}\text{-tolyl})\}}]_6$ (1.76(3) Å)[13] and $[\mathrm{Cu_{28}(H)_{15}\{S_2CN(^nPr)_2\}_{12}}](\mathrm{PF_6})$ (avg 1.71(4) Å). The Cu−(near square-planar μ_4-H) distances, which exhibit a range of 1.82(2) Å−1.90(2) Å (1.87(5) Å avg), are slightly longer than the Cu−(face-capping μ_3-H) distances. In the DFT model, a similar trend is also observed for the Cu−(μ_4-$\mathrm{H_{nsp}}$) distances (avg 1.84 Å) and Cu−(μ_3-H) distances (avg 1.72 Å). The increased coordination number of the hydride from μ_3 to μ_4 reflects a decrease of the bond order, which results in an increase of the Cu−H distances. A similar trend was also apparent among yttrium-hydride distances, where $\mathrm{Y_2}$−(μ_2-H) and $\mathrm{Y_3}$−(μ_3-H) exhibited an increased Y−H distance (i.e., 2.168(9) Å and 2.345(8) Å, respectively).[8f] Moreover, a gradual increase in the Co−H distance (i.e., 1.558(18) Å, 1.641(6) Å, 1.734(4) Å, 1.823(13) Å) has been reported to occur in the series Co−H (terminal), $\mathrm{Co_2}$(μ_2-H), $\mathrm{Co_3}$(μ_3-H), and $\mathrm{Co_6}$(μ_6-H), respectively.[7a] In $[\mathrm{Cu_{28}(H)_{15}\{S_2CN(^nPr)_2\}_{12}}](\mathrm{PF_6})$,[11] the distance between Cu and the truncating hydride (i.e., μ_6-H and μ_5-H, avg 1.94(10) Å) is significantly longer than the Cu−(μ_3-H) distances (avg 1.71(4) Å).

Interestingly, the distances between Cu and tetrahedral hydride (μ_4-$\mathrm{H_{Td}}$), which were observed to range from 1.61(1) Å to 1.752(9) Å (avg 1.71(2) Å), did not follow this trend, even though the average bond length of 1.56(5) Å for (Cu−μ_4-$\mathrm{H_{Td}}$) in $[\mathrm{Cu_{28}(H)_{15}\{S_2CN(^nPr)_2\}_{12}}](\mathrm{PF_6})$ is considerably shorter than expected. In contrast, this bond length was expected to be longer (i.e., 1.86(2) Å) in $[\mathrm{Cu_4}(\mu_4\text{-H})(\mu_3\text{-Cu})_3\{\mathrm{S_2C}(\text{aza-15-crown-5})\}_6]$. Indeed, 4-coordinate hydrides do exist in solid-state copper(I) hydride (CuH), the first binary metal hydride.[14] Its wurtzite-type structure was established by Müller and Bradly in 1926;[15] in 1955, Goedkoop and Andresen used powder neutron diffraction to confirm its Cu−H bond distances of 1.73 Å.[16] However, the four-coordinated hydride in both $[\mathrm{Cu_7(H)}\{\mathrm{S_2C}(\text{aza-15-crown-5})\}_6]$,[10a] which has a 3-fold elongated $\mathrm{Cu_4}$ core, and $[\mathrm{Cu_{28}(H)_{15}\{S_2CN(^nPr)_2\}_{12}}]^+$,[11] whose central $\mathrm{Cu_4}$ unit exhibits a disorder over three perpendicular orientations, makes the comparison of Cu−$\mathrm{H_{Td}}$ distances less meaningful. Clearly, two tetrahedral hydrides in a $\mathrm{Cu_{20}}$ cluster are more restricted because of the environment of the $\mathrm{Cu_4}$ array. Thus, four copper atoms in a tetrahedral array make the interstitial hole smaller than that in a square-planar array. Three sets of $\mathrm{Cu_4H}$, which share an edge formed by the centered Cu atoms, constitute a $\mathrm{Cu_8H_3}$ motif (Figure 3a) of the hexagonal prismatic fragment of the $\mathrm{Cu_{20}H_{11}}$ core (Figure 2b). The three remarkable four-coordinated hydrides, i.e., H9M, H10M, and H11M, were located slightly above the $\mathrm{Cu_4}$ square plane, at distances of 0.270(15) Å, 0.231(16) Å, and 0.308(15) Å, respectively (Figure 3b). For comparison, the hydride atoms are located 0.136 Å, 0.140 Å, and 0.139 Å away from the $\mathrm{Cu_4}$ square plane in the DFT model. For each of the four-coordinated hydrides, the four DFT Cu−H bond distances split into two shorter (1.78 Å) and two longer (1.90 Å) values, whereas the four Cu−H bond distances determined by neutron diffraction are essentially equivalent. These differences are attributed to the level of sophistication of the calculations. The time-averaged positions of the $\mathrm{H_{nsp}}$ atoms, as determined from their thermal vibrations, indicate that the $\mathrm{Cu_4}$ square plane actually possesses sufficient space to allow the hydrides to move. The near square-planar geometry of the four-coordinated hydrides determined from the DFT calculations is in good agreement with that observed in the structure obtained by neutron diffraction. The omit map in Figure 4(a) shows the distribution of negative nuclear densities for each of the three hydrides that penetrate the individual plane defined by each set of four copper atoms, despite the fact that each of the hydrogen atoms from the structure refinement is located slightly above the $\mathrm{Cu_4}$ plane (Figure 4(b)). The sums of the vertex angles at H9M, H10M, and H11 M are 355.2(7)°, 356.4(7)°, and 353.9(6)°, respectively. On the basis of the aforementioned

Table 2. Cu−H Distances from Both Neutron Data and DFT Calculation

	Neutron data	DFT calculation
	Cu−(tetrahedral H) Distances	
H1M-Cu1	1.73(1)	1.740
H1M-Cu2	1.75(1)	1.739
H1M-Cu3	1.75(1)	1.740
H1M-Cu19	1.615(9)	1.622
H2M-Cu16	1.74(1)	1.740
H2M-Cu17	1.75(1)	1.739
H2M-Cu18	1.73(1)	1.739
H2M-Cu20	1.61(1)	1.622
	Cu−(triangular face-capping H) Distances	
H3M-Cu2	1.67(1)	1.685
H3M-Cu5	1.70(1)	1.715
H3M-Cu6	1.75(1)	1.769
H4M-Cu1	1.67(1)	1.681
H4M-Cu4	1.72(2)	1.772
H4M-Cu9	1.68(1)	1.714
H5M-Cu3	1.67(1)	1.685
H5M-Cu7	1.70(1)	1.711
H5M-Cu8	1.75(1)	1.774
H6M-Cu11	1.72(1)	1.715
H6M-Cu12	1.75(2)	1.769
H6M-Cu17	1.65(1)	1.685
H7M-Cu10	1.77(1)	1.772
H7M-Cu15	1.72(2)	1.714
H7M-Cu16	1.66(1)	1.681
H8M-Cu13	1.70(1)	1.711
H8M-Cu14	1.75(1)	1.774
H8M-Cu18	1.68(1)	1.685
	Cu−(near-square planar H) Distances	
H9M-Cu4	1.90(2)	1.778
H9M-Cu10	1.88(2)	1.778
H9M-Cu19	1.82(2)	1.896
H9M-Cu20	1.87(1)	1.896
H10M-Cu8	1.86(2)	1.778
H10M-Cu14	1.86(1)	1.778
H10M-Cu19	1.87(1)	1.896
H10M-Cu20	1.83(2)	1.896
H11M-Cu6	1.84(1)	1.781
H11M-Cu12	1.88(2)	1.781
H11M-Cu19	1.89(1)	1.893
H11M-Cu20	1.88(1)	1.893

structural elucidation, the coordination environment of the μ_4-H is very close to square planar. Thus, to the best of our knowledge, *$[Cu_{20}(H)_{11}\{S_2P(O^iPr)_2\}_9]$ possesses the first four-coordinated hydride of near square-planar geometry fully supported by single-crystal neutron diffraction.*

The Cu⋯Cu distances determined from X-ray data, neutron data, and the DFT model do not substantially differ. The Cu⋯Cu distances are listed in Supporting Information Table S1. The average edge length (2.780(16) Å) of a Cu_4 tetrahedron with an interstitial hydride is much shorter than the average edge length (3.01(3) Å) of a Cu_4 tetrahedron in $[Cu_7(H)\{S_2C(\text{aza-15-crown-5})\}_6]$, which is a consequence of the pseudo-C_3 elongation to form a larger Cu_4 tetrahedron. The distance of 2.302(7) Å between the two inner copper atoms is now the shortest Cu⋯Cu distance reported in the Cambridge Structural Database (v. 5.34). Relatedly, we note that two very short Cu⋯Cu distances of 2.305(1) Å and 2.3058(5) Å were determined in NHC-stabilized dinuclear copper hydrides.[17]

■ CONCLUSIONS

In summary, an air-stable polyhydrido copper cluster, $[Cu_{20}(H)_{11}\{S_2P(O^iPr)_2\}_9]$, was successfully characterized by neutron diffraction experiments on a tiny crystal (~0.065 mm^3) of excellent quality. The analysis of the compound reveals μ_3-H in a pyramidal geometry, μ_4-H in a tetrahedral cavity, and μ_4-H in a near square-planar geometry. Importantly, this compound is the first metal hydride that displays an unprecedented near square-planar hydride coordination geometry. The distance between the inner copper atoms is remarkably short, indicating a strong $d^{10}-d^{10}$ cuprophilic interaction. Thus, in addition to the interstitial hydrides being characterized by single-crystal neutron diffraction techniques,[10a,11] this contribution strongly suggests that the presence of hydride in reduction-derived noble-metal nanoclusters must be taken into account when determining their total structures.

■ EXPERIMENTAL SECTION

Synthesis of $[Cu_{20}(H)_{11}\{S_2P(O^iPr)_2\}_9]$. In a flame-dried Schlenk tube, $NH_4[S_2P(O^iPr)_2]$ (0.139 g, 0.60 mmol) and $[LiBH_4{\cdot}THF]$ (0.8 mL, 1.6 mmol) were mixed in THF (20 mL). After the mixture was cooled to 0 °C, a $[Cu(CH_3CN)_4]PF_6$ (0.490 g, 1.31 mmol) solution in THF (10 mL) was added. The resulting solution was stirred for 5 h at 10 °C and then dried under vacuum; then dried residue was subsequently dissolved in CH_2Cl_2 and washed with water (2 × 15 mL). The organic layer was separated, filtered, and dried. Methanol (2 × 15 mL) was added to the brown residue, and the resulting turbid solution was cooled in a freezer to approximately −4 °C (repeated in duplicate) for several hours, which resulted in the formation of a yellow precipitate. The precipitate was dissolved in ether, filtered, and evaporated to dryness, yielding a pure light-yellow powder of $[Cu_{20}(H)_{11}\{S_2P(O^iPr)_2\}_9]$, $\mathbf{1_H}$ (0.100 g, 48% based on Cu).

Preparation of Crystals. The yellow crystals were grown by slow diffusion of hexane into benzene in a refrigerator at 10 °C. The large crystals were collected and transferred to a thickened glass tube to which a small amount of benzene solvent and N_2 gas were subsequently added. The tube was then sealed and shipped to ORNL for the neutron diffraction experiment.

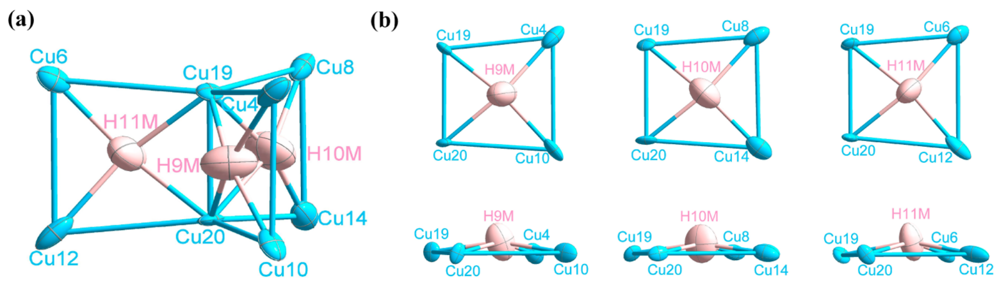


Figure 3. (a) Cu_8H_3 motif view of a $Cu_{20}H_{11}$ core with three Cu_4H squares sharing an edge. (b) Two orientations of each Cu_4H square.

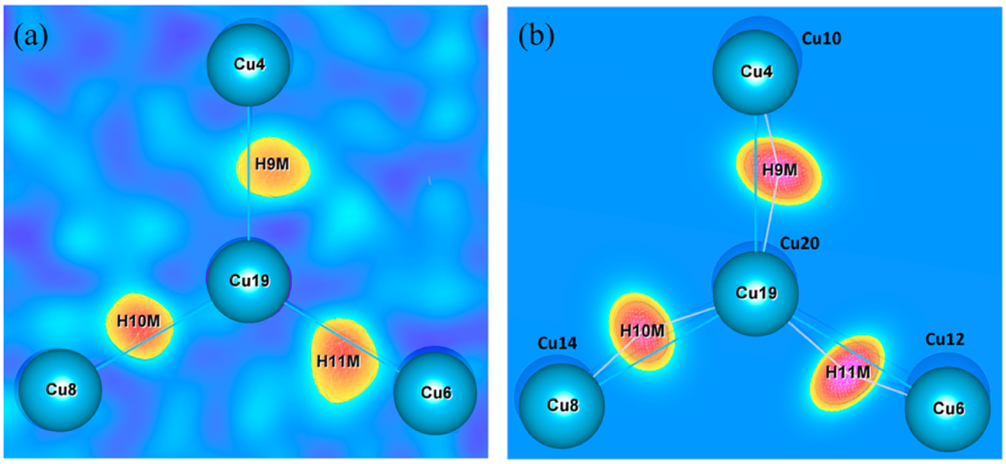


Figure 4. (a) Difference Fourier section showing the negative nuclear densities in the omit map with the near square-planar coordinated hydrides H9M, H10M, and H11M removed from the crystal structure of $[Cu_{20}(H)_{11}\{S_2P(O^iPr)_2\}_9]$. (b) Corresponding model nuclear densities showing the displacements of the three hydrides H9M, H10M, and H11M from each of the Cu_4-squares defined by [Cu4,Cu10,Cu19,Cu20], [Cu8,Cu14,Cu19,Cu20], and [Cu6,Cu12,Cu19,Cu20], respectively. The nuclear densities are shown with an isosurface level of −4 fm Å.

Single-Crystal Neutron Diffraction. The single-crystal neutron diffraction experiment was performed using the TOPAZ single-crystal time-of-flight Laue diffractometer at the Spallation Neutron Source, Oak Ridge National Laboratory.[18] A plate-shaped crystal of polyhydrido copper cluster, $[Cu_{20}(H)_{11}\{S_2P(O^iPr)_2\}_9]\cdot 1.5$(benzene) ($\mathbf{1_N}$), with the dimensions of 0.20 × 0.50 × 0.65 mm^3 was mounted onto the tip of a polyimide capillary using fluorinated grease and was subsequently transferred onto the TOPAZ goniometer for data collection at 100 K. To ensure good coverage and redundancy, data were collected using 28 crystal orientations optimized with the CrystalPlan software[19] for an estimated 97% coverage of symmetry-equivalent reflections of the triclinic cell. Each orientation was measured for approximately 6 h. The integrated raw Bragg intensities were obtained using the 3-D ellipsoidal *Q*-space integration method in Mantid.[20] Data reduction, including the neutron TOF spectrum, detector efficiency, and absorption corrections, was carried out with the ANVRED2 program.[21] The reduced data were saved in the SHELX HKLF2 file format, which records the wavelength separately for each individual reflection; thus, the wavelength and reflections were not merged as a result of this saved format. The initial structural model used the non-hydrogen atom positions determined from a single-crystal XRD measurement. The hydrogen atoms on the isopropyl groups were refined with geometry constraints. The metal hydrides were determined from the nuclear difference Fourier map of the neutron data and were refined anisotropically using SHELXL-97[22] in WinGx.[23] Four isopropyl groups and one of the benzene solvent molecules were observed to be disordered in two positions and were refined isotropically with distance constraints. The neutron structure was validated with the Platon and IUCr online checkcif programs.[24]

Computational Details. Density functional theory (DFT) calculations were performed on the simplified model $Cu_{20}(H)_{11}(S_2PH_2)_9$ using the Gaussian 09 software package[25] and employing the BP86 exchange-correlation functional.[26] Geometry optimizations were first performed with the general double-ξ polarized LANL2DZ basis set[27a−d] augmented with Ahlrichs polarization functions on all atoms[27e] and were then refined with the general triple-ξ polarized basis set Def2-TZVPP from the EMSL Basis Set Exchange Library.[28] An all-electron basis set was used for copper. The optimized geometry was characterized as a true minimum via analytical frequency calculations. The optimized geometry of $Cu_{20}(H)_{11}(S_2PH_2)_9$ was observed to be very close to C_{3h} symmetry. Among the different hydride locations (edge- or face-bridging) examined from the starting geometries, this symmetrical structure was the only low-energy minimum found.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Tables of selected bond lengths, computational result, and neutron crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org. CCDC 1014790 contains the supplementary neutron crystallographic data of $[Cu_{20}(H)_{11}\{S_2P(O^iPr)_2\}_9]$.

■ AUTHOR INFORMATION

Corresponding Author

* E-mail: chenwei@mail.ndhu.edu.tw. Tel: +886-3-8633607. Fax: +886-3-8633570.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Dedicated to Professor John P. Fackler, Jr. on the occasion of his 80th birthday. This work was supported by the Ministry of Science and Technology of Taiwan (MOST 103-2113-M-259-003-MY3). The neutron single crystal diffraction measurement was carried out at the ORNL Spallation Neutron Source, which is sponsored by the Division of Scientific User Facilities, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract No. DE-AC05-00OR22725 with UT-Battelle, LLC.

■ REFERENCES

(1) (a) Mueller, W. M.; Blackledge, J. P.; Libowitz, G. G. In *Metal Hydrides*; Academic Press: New York and London, 1968. (b) Dedieu, A. In *Transition Metal Hydrides*; Wiley-VCH: Weinheim, Germany, 1992. (c) Poli, R.; Peruzzini, M. In *Recent Advances in Hydride Chemistry*; Amsterdam, 2001; p 557.

(2) (a) Kaesz, H. D.; Saillant, R. B. *Chem. Rev.* **1972**, *72*, 231. (b) Lin, Z.; Hall, M. B. *Coord. Chem. Rev.* **1994**, *135*, 845. (c) Sabo-Etienne, S.; Chaudret, B. *Coord. Chem. Rev.* **1998**, *178*, 381. (d) Maseras, F.; Lledos, A.; Clot, E.; Eisenstein, O. *Chem. Rev.* **2000**, *100*, 601. (e) King, R. B. *Coord. Chem. Rev.* **2000**, *200–202*, 813. (f) Hoskin, A. J.; Stephan, D. W. *Coord. Chem. Rev.* **2002**, *233–234*, 107. (g) Morris, R. H. *Coord. Chem. Rev.* **2008**, *252*, 2381. (h) Holland, P. L. *Acc. Chem. Res.* **2008**, *41*, 905. (i) Gloaguen, F.; Rauchfuss, T. B. *Chem. Soc. Rev.* **2009**, *38*, 100.

(3) (a) Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. *J. Chem. Soc., A: Inorg. Phys. Theor.* **1966**, 1711. (b) Angelici, R. J. *Acc.*

Chem. Res. **1988**, *21*, 387. (c) Brestensky, D. M.; Stryker, J. M. *Tetrahedron Lett.* **1989**, *30*, 5677. (d) Miller, K. M.; Luanphaisarnnont, T.; Molinaro, C.; Jamison, T. F. *J. Am. Chem. Soc.* **2004**, *126*, 4130. (e) Brayshaw, S. K.; Harrison, A.; McIndoe, J. S.; Marken, F.; Raithby, P. R.; Warren, J. E.; Weller, A. S. *J. Am. Chem. Soc.* **2007**, *129*, 1793.

(4) (a) Sakintuna, B.; Lamari-Dakrim, F.; Hirscher, M. *Int. J. Hydrogen Energy* **2007**, *32*, 1121. (b) Bogdanović, B.; Schwickardi, M. *J. Alloys Compd.* **1997**, *253−254*, 1. (c) Schlapbach, L.; Züttel, A. *Nature* **2001**, *414*, 353. (d) Fukuzumi, S.; Suenobu, T. *Dalton Trans.* **2013**, *42*, 18.

(5) (a) Bau, R.; Drabnis, M. H. *Inorg. Chim. Acta* **1997**, 27. (b) Piccoli, P. M. B.; Koetzle, T. F.; Schultz, A. J. *Comments Inorg. Chem.* **2007**, *28*, 3.

(6) *Neutron News* **1992**, Vol. 3, (3), pp 29−37.

(7) (a) Lutz, F.; Bau, R.; Wu, P.; Koetzle, T. F.; Krüger, C.; Schneider, J. J. *Inorg. Chem.* **1996**, *35*, 2698. (b) Teller, R. G.; Wilson, R. D.; McMullan, R. K.; Koetzle, T. F.; Bau, R. *J. Am. Chem. Soc.* **1978**, *100*, 3071. (c) Hart, D. W.; Teller, R. G.; Wei, C. Y.; Bau, R.; Longoni, G.; Campanella, S.; Chini, P.; Koetzle, T. F. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 80. (d) Hart, D. W.; Teller, R. G.; Wei, C. Y.; Bau, R.; Longoni, G.; Campanella, S.; Chini, P.; Koetzle, T. F. *J. Am. Chem. Soc.* **1981**, *103*, 1458. (e) Bau, R.; Drabnis, M. H.; Garlaschelli, L.; Klooster, W. T.; Xie, Z.; Koetzle, T. F.; Martinengo, S. *Science* **1997**, *275*, 1099. (f) Broach, R. W.; Dahl, L. F.; Longoni, G.; Chini, P.; Schultz, A. J.; Williams, J. M. *Adv. Chem. Ser.* **1979**, *167*, 93.

(8) (a) Tardif, O.; Nishiura, M.; Hou, Z. *Organnometallics* **2003**, *22*, 1171. (b) Cui, D.; Tardif, O.; Hou, Z. *J. Am. Chem. Soc.* **2004**, *126*, 1312. (c) Cui, D.; Nishiura, M.; Hou, Z. *Angew. Chem., Int. Ed.* **2005**, *44*, 959. (d) Li, X.; Baldamus, J.; Nishiura, M.; Tardif, O.; Hou, Z. *Angew. Chem., Int. Ed.* **2006**, *45*, 8184. (e) Hou, Z.; Nishiura, M.; Shima, T. *Eur. J. Inorg. Chem.* **2007**, 2535. (f) Yousufuddin, M.; Gutmann, M. J.; Baldamus, J.; Tardif, O.; Hou, Z.; Mason, S. A.; McIntyre, G. J.; Bau, R. *J. Am. Chem. Soc.* **2008**, *130*, 3888. (g) Takenaka, Y.; Shima, T.; Baldamus, J.; Hou, Z. *Angew. Chem., Int. Ed.* **2009**, *48*, 7888. (h) Shima, T.; Nishiura, M.; Hou, Z. *Organometallics* **2011**, *30*, 2513. (i) Zhang, W.-X.; Wang, Z.; Nishiura, M.; Xi, Z.; Hou, Z. *J. Am. Chem. Soc.* **2011**, *133*, 5712. (j) Hong, J.; Zhang, L.; Yu, X.; Li, M.; Zhang, Z.; Zheng, P.; Nishiura, M.; Hou, Z.; Zhou, X. *Chem.—Eur. J.* **2011**, *17*, 2130. (k) Shima, T.; Luo, Y.; Stewart, T.; Bau, R.; McIntyre, G. J.; Mason, S. A.; Hou, Z. *Nat. Chem.* **2011**, *3*, 814.

(9) (a) Liao, P.-K.; Sarkar, B.; Chang, H.-W.; Wang, J.-C.; Liu, C. W. *Inorg. Chem.* **2009**, *48*, 4089. (b) Liu, C. W.; Sarkar, B.; Huang, Y.-J.; Liao, P.-K.; Wang, J.-C.; Saillard, J.-Y.; Kahlal, S. *J. Am. Chem. Soc.* **2009**, *133*, 11222. (c) Liu, C. W.; Chang, H.-W.; Sarkar, B.; Saillard, J.-Y.; Kahlal, S.; Wu, Y.-Y. *Inorg. Chem.* **2010**, *49*, 468. (d) Liu, C. W.; Chang, H.-W.; Fang, C.-S.; Sarkar, B.; Wang, J.-C. *Chem. Commun.* **2010**, *46*, 4571. (e) Liao, P.-K.; Liu, K.-G.; Fang, C.-S.; Liu, C. W.; Fackler, J. P., Jr.; Wu, Y.-Y. *Inorg. Chem.* **2011**, *50*, 8410. (f) Liao, P.-K.; Shi, D.-R.; Liao, J.-H.; Liu, C. W.; Artemev, A. V.; Kuimov, V. A.; Gusarova, N. K.; Trofimov, B. A. *Eur. J. Inorg. Chem.* **2012**, 4921. (g) Latouche, C.; Liu, C. W.; Saillard, J.-Y. *J. Clust. Sci.* **2014**, *25*, 147.

(10) (a) Liao, P.-K.; Fang, C.-S.; Edward, A. J.; Kahlal, S.; Saillard, J.-Y.; Liu, C. W. *Inorg. Chem.* **2012**, *51*, 6577. (b) Latouche, C.; Kahlal, S.; Lin, Y.-R.; Liao, J.-H.; Furet, E.; Liu, C. W.; Saillard, J.-Y. *Inorg. Chem.* **2013**, *52*, 13253.

(11) Edwards, A. J.; Dhayal, R. S.; Liao, P.-K.; Liao, J.-H.; Chiang, M.-H.; Piltz, R. O.; Kahlal, S.; Saillard, J.-Y.; Liu, C. W. *Angew. Chem., Int. Ed.* **2014**, *53*, 7214−7218.

(12) Dhayal, R. S.; Liao, J.-H.; Lin, Y.-R.; Liao, P.-K.; Kahlal, S.; Saillard, J.-Y.; Liu, C. W. *J. Am. Chem. Soc.* **2013**, *135*, 4704.

(13) (a) Stevens, R. C.; McLean, M. R.; Bau, R. *J. Am. Chem. Soc.* **1989**, *111*, 3472. (b) Bennett, E. L.; Murphy, P. J.; Imberti, S.; Parker, S. F. *Inorg. Chem.* **2014**, *53*, 2963. As noted by Parker *et al.* based on the inelastic neutron scattering study of Stryker's reagent, $[HCu\{P(C_6H_5)_3\}]_6$, the location of hydrides in the Cu_6 core may be best described as the edge-bridging (μ_2-H) rather than triply bridging (μ_3-H) as reported by Bau *et al.* on the *p*-tolyl derivative.

(14) Wurtz, A. *C. R. Hebd. Seances Acad. Sci.* **1844**, *18*, 702.

(15) Müller, H.; Bradley, A. J. *J. Chem. Soc.* **1926**, 1669.

(16) Goedkoop, J. A.; Andresen, A. F. *Acta Crystallogr.* **1955**, *8*, 118.

(17) (a) Mankad, N. P.; Laitar, D. S.; Sadighi, J. P. *Organometallics* **2004**, *23*, 3369. (b) Frey, G. D.; Donnadieu, B.; Soleilhavoup, M.; Bertrand, G. *Chem.−Asian J.* **2011**, *6*, 402.

(18) Jogl, G.; Wang, X.; Mason, S. A.; Kovalevsky, A.; Mustyakimov, M.; Fisher, Z.; Hoffman, C.; Kratky, C.; Langan, P. *Acta Crystallogr., Sect. D* **2011**, *67*, 584.

(19) Zikovsky, J.; Peterson, P. F.; Wang, X.; Frost, M.; Hoffmann, C. *J. Appl. Crystallogr.* **2011**, *44*, 418.

(20) Schultz, A. J.; Jorgensen, M. R. V.; Wang, X.; Mikkelson, R. L.; Mikkelson, D. J.; Lynch, V. E.; Peterson, P. F.; Green, M. L.; Hoffmann, C. *J. Appl. Crystallogr.* **2014**, *47*, 915.

(21) Schultz, A. J.; Srinivasan, K.; Teller, R. G.; Williams, J. M.; Lukehart, C. M. *J. Am. Chem. Soc.* **1984**, *106*, 999.

(22) Sheldrick, G. *Acta Crystallogr., Sect. A* **2008**, *64*, 112.

(23) Farrugia, L. *J. Appl. Crystallogr.* **2012**, *45*, 849.

(24) Spek, A. *J. Appl. Crystallogr.* **2003**, *36*, 7.

(25) *Gaussian 09*, Revision A.1; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G. ; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc.: Wallingford, CT, 2009M.

(26) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.

(27) (a) Dunning, T. H., Jr.; Hay, P. J. In *Methods of Electronic Structure Theory*; Schaeffer, H. F., Eds.; Plenum Press: New York, 1977. (b) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270. (c) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 284. (d) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299. (e) Schafer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571.

(28) Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.