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Facile Entrapment of a Hydride inside the Tetracapped Tetrahedral Cu^I_8 Cage Inscribed in a S_{12} Icosahedral Framework

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Reaction of $[Cu(CH_3CN)_4](PF_6)$ and $NH_4[S_2P(OR)_2]$ in a 4:3 ratio in acetone at room temperature produces octanuclear dicationic copper complexes $[Cu_8\{S_2P(OR)_2\}_6](PF_6)_2$ (R = ^{i}Pr, **1**; Et, **3**) in 81 and 83% yields, respectively. On the other hand, reaction of $[Cu(CH_3CN)_4](PF_6)$, $NH_4[S_2P(OR)_2]$, and $NaBH_4$ in an 8:6:1 molar ratio in THF for 1 h yields $[Cu_4(H)(\mu_3\text{-}Cu)_4\{S_2P(OR)_2\}_6](PF_6)$ (R = ^{i}Pr, **2a**; Et, **4a**) in 87 and 82% yields, respectively. In a similar reaction when $NaBD_4$ is used instead of $NaBH_4$, $[Cu_4(D)(\mu_3\text{-}Cu)_4\{S_2P(OR)_2\}_6](PF_6)$ (R = ^{i}Pr, **2b**; Et, **4b**) are obtained in 83 and 78% yields, respectively. Structural elucidations of **2a** and **4a** reveal the tetracapped tetrahedral Cu_8 cage with an interstitial hydride. Each of the Cu(I) centers is trigonally coordinated by three S atoms, and each of the six dithiophosphate ligands is connected to a Cu_4 butterfly, where the hinge positions are occupied by two copper atoms situated at the vertex of the central tetrahedron and the wingtips are two capping Cu atoms. The 12 S atoms out of the six ligands constitute an icosahedron around the hydride-centered tetracapped tetrahedral Cu_8 framework. Surprisingly, empty Cu_8 clusters **1** and **3** can abstract hydride (or deuteride) from $NaBH_4$ (or $NaBD_4$) in THF to form **2a** and **4a** (or **2b** and **4b**), respectively. Apparently the cubic Cu_8 core, which is known to be formed in the reaction of Cu(I) salt and dichalcogenophosph(in)ate ligands, undergoes a tetrahedral contraction due to the strong $Cu\cdots H$ interactions. Interestingly, the chloride can also be replaced from the chloride-centered Cu_8 complex of $[Cu_8(Cl)\{S_2P(OEt)_2\}_6](PF_6)$ by hydride (or deuteride) to form **2a** and **4a** (or **2b** and **4b**). However, the hydride- and deuteride-centered compounds **2a**,**b** and **4a**,**b** do not allow the guest exchange.

Introduction

Since Birker and Freeman reported the first, mixed-valence copper cluster, $Cu^I_8Cu^{II}_6(Cl)(\text{D-Pen})_{12}^{5-}$,[1] in which structural elucidation was intended to lead to understanding of the role of D-penicillamine in the treatment of Wilson disease caused by the pathological accumulation of copper in the liver and brain,[2] research efforts have endeavored to isolate the central portion of the cluster, namely, the anion-centered cubic copper cluster due to the importance of anion coordination chemistry[3] and unusual bonding characteristics.[4] Several sulfide- and selenide-centered cubic copper clusters incorporating monoanionic dichalcogenophosph(in)ato ligands [$E_2P(OR)_2^-$, $E_2PR_2^-$; E = S, Se] were isolated from the reaction of copper salts with the corresponding ligands.[5] In the presence of chloride and bromide, cubic copper clusters encapsulating a halide anion could be isolated.[6] The general structural feature of these molecules can be described as an anion-centered cubic copper framework inscribed in a slightly distorted E_{12} icosahedral cage having an idealized T_h point group symmetry. To our great surprise, the hydride-centered

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cubic copper cluster has never been isolated, even though the 1s orbital of hydride, a totally symmetric one, appears to match well with the symmetry of linear combinations of the eight p orbitals, each perpendicular to the trigonal-planar Cu(I) atoms in the T_h symmetry.[4a]

On the other hand, since Churchill et al. reported hexanuclear Cu(I) complex $[HCuPPh_3]_6$ in 1971,[7] several reports appeared in the literature involving hydrides coordinated to the Cu cluster, mostly from the outer surface of the metallic core. Nevertheless, the smallest closed-shell anion, the hydride, entrapped inside a Cu_x (x >3) cage, is scarce. To the best of our knowledge, only a single structurally characterized compound, $[Cu_6(H)(Cl)\{Me_3(NCH_2)_3\}_3]^+$,[8] in which the hydride ion is trapped inside an octahedral Cu_6^I cage is known. Also, Che's group has reported structures of trinuclear copper complexes where a hydride was sitting inside a Cu_3 plane.[9] However, none of the Cu−H clusters involving phosphorochalcogenides as the supporting ligand have been reported.

Although the hydrogen content of a hydride-encapsulated metal complex is limited, research on hydrogen storage in metal complexes, which is turning on the possibilities of activated light metal hydrides to act as hydrogen sources,[10] contributes more significance to the study of hydride entrapment within metals. On the other hand, anion recognition by metal complexes has attracted much attention over the past two decades.[11] Unlike the chloride, bromide, or chalcogenide, entrapment of a hydride inside metal clusters is not very common. For example, Hou et al. reported Y(III), Lu(III), and Sm(III) complexes in which bridging hydrides constitute the basic framework along with a H^- anion inside the tetrahedral cage.[12] An interstitial hydride inside the cubic Li_8 cage was reported by the Wheatley group, involving bridging N-donor ligands.[13] Aside from the copper complex mentioned above,[8] Kamiguchi also reported $[Cr_6(H)(S_8)(PEt_3)_5]_2$ and $[Cr_6(H)(S_8)(PEt_3)_6]^+$ containing an interstitial hydride inside the octahedral Cr_6 cage.[14] None of them displayed a tetracapped tetrahedral metallic core.

Metal complexes of 1,1-dithioate ligands, which have diverse applications such as rubber vulcanization accelerators, fungicides, and lubricant additives,[15] can also be employed to form Cu clusters.[16] Herein, the high-yield syntheses of $[Cu_8\{S_2P(OR)_2\}_6]^{2+}$ (R = ^{i}Pr, **1**; Et, **3**) and $[Cu_4(\mu_4\text{-}X)(\mu_3\text{-}Cu)_4\{S_2P(OR)_2\}_6]^+$ (R = ^{i}Pr; X = H, **2a**, X = D, **2b**; R = Et; X = H, **4a**, X = D, **4b**) with the structural elucidations of both **2a** and **4a** have been reported. The new, hydride-centered compound can be obtained directly from the copper salt, 1,1-dithioate ligand, and sodium borohydride in an 8:6:1 ratio. Subsequently, the hydride-/deuteride-centered Cu_8 clusters (**2a**,**b** and **4a**,**b**) can also be prepared from a stoichiometric amount of $NaBH_4$ (or $NaBD_4$) and the empty cluster, $Cu_8[S_2P(OR)_2]_6^{2+}$, **1** (or **3**) in excellent yield, as evident from the ^{31}P NMR studies.

Experimental Section

All of the solvents, namely, acetone, dichloromethane, and THF, were purchased from Mallinckrodt Chemicals and purified before use following standard procedures.[17] Other reagent-grade chemicals were purchased from Aldrich and used without further purification. All of the reactions were carried out under an inert atmosphere using a Schlenk apparatus. Elemental analyses were done using a Heraeus VarioEL-III CNH analyzer. Multinuclear (^{1}H, ^{31}P) NMR spectra were recorded with a Bruker Advance DPX300 FT-NMR spectrometer. The NMR spectrometer was operated at 300.130 MHz for recording ^{1}H NMR spectra, whereas it was operated at 46.072 MHz for ^{2}H NMR and at 121.495 MHz for ^{31}P NMR. The $^{31}P\{^1H\}$ NMR spectra were referenced externally against 85% H_3PO_4 (δ = 0 ppm). $NH_4S_2P(O^iPr)_2$ was prepared by following the method reported by Wystrach et al.,[18] whereas $NH_4S_2P(OEt)_2$ was obtained

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from Aldrich. $Cu(CH_3CN)_4PF_6$ was synthesized following the literature procedure.[19]

Synthesis. $[Cu_8\{S_2P(O^iPr)_2\}_6](PF_6)_2$, 1. $Cu(CH_3CN)_4PF_6$ (0.432 g, 1.16 mmol) and $NH_4[S_2P(O^iPr)_2]$ (0.201 g, 0.87 mmol) were charged in a 100 mL Schlenk flask. A total of 30 mL of acetone was added to it, and the solution was stirred at room temperature for 1 h. It was then filtered to get rid of any solid, and the filtrate was evaporated to dryness under a vacuum to get a colorless solid. The solid was washed with deionized water to remove any NH_4PF_6 formed during the reaction and dried under a vacuum to obtain $Cu_8[S_2P(O^iPr)_2]_6(PF_6)_2$ as a white powder. Yield: 0.245 g (81%). Mp: 153 °C. Anal. calcd for $Cu_8H_{84}C_{36}O_{12}P_8F_{12}S_{12}\cdot 0.5[(CH_3)_2CO]$: C, 21.38; H, 4.16. Found: C, 21.40; H, 4.50%. ^1H NMR (acetone-d_6, δ, ppm): 1.47 (d, $^3J_{HH} = 6$ Hz, 72H, CH_3), 5.07 (m, 12H, OC*H*). ^{31}P NMR (acetone-d_6, δ, ppm): 88.8, −143.0 (septet, $^2J_{PF} = 707.6$ Hz). MALDI-TOF MS (*m*/*z*): 892.80 (894.0 for $[Cu_8\{S_2P(O^iPr)_2\}_6]^{2+}$).

$[Cu_4(H)(\mu_3\text{-}Cu)_4\{S_2P(O^iPr)_2\}_6](PF_6)$, 2a. $Cu(MeCN)_4PF_6$ (0.417 g, 1.12 mmol), $NH_4[S_2P(O^iPr)_2]$ (0.194 g, 0.84 mmol), and $NaBH_4$ (0.005 g, 0.14 mmol) were charged in a 100 mL Schlenk flask. A total of 30 mL of THF was added to it and stirred at room temperature for 30 min. The reaction mixture was filtered, and the filtrate was evaporated to dryness under a vacuum to obtain a brown solid. The solid was washed with deionized water and dried under a vacuum to get $[Cu_4(\mu_4\text{-}H)(\mu_3\text{-}Cu)_4\{S_2P(O^iPr)_2\}_6](PF_6)$ as a brown powder. Yield: 0.234 g (87%). Mp: 168 °C. Anal. calcd for $Cu_8H_{85}C_{36}O_{12}P_7F_6S_{12}\cdot 2H_2O$: C, 21.95; H, 4.55. Found: C, 21.91; H, 4.60%. ^1H NMR (acetone-d_6, δ, ppm): 1.42 (d, $^3J_{HH} = 5.9$ Hz, 72H, CH_3), 3.69 (bs, 1H, μ_4-H), 4.89 (m, 12H, OC*H*). ^{31}P NMR (acetone-d_6, δ, ppm): 100.4, −143.0 (septet, $^2J_{PF} = 707.6$ Hz). MALDI-TOF MS (*m*/*z*): 1787.9 (1789.0 for $[Cu_8(H)\{S_2P(O^iPr)_2\}_6]^+$), 892.63 ($[Cu_8\{S_2P(O^iPr)_2\}_6]^{2+}$).

$[Cu_4(D)(\mu_3\text{-}Cu)_4\{S_2P(O^iPr)_2\}_6](PF_6)$, 2b. Compound **2b** was prepared in a similar fashion to **1a** by using $NaBD_4$ instead of $NaBH_4$. Yield: 0.224 g (83%). Mp: 170 °C. Anal. calcd for $Cu_8H_{84}DC_{36}O_{12}P_7F_6S_{12}\cdot 5H_2O$: C, 21.35; H, 4.78. Found: C, 21.13; H, 4.46. ^1H NMR (acetone-d_6, δ, ppm): 1.43 (d,$^3J_{HH} = 6.1$ Hz, 72H, CH_3), 4.90 (m, 12H, OC*H*). ^2H NMR (acetone-d_6, δ, ppm): 3.71 (bs, 1D). ^{31}P NMR (acetone-d_6, δ, ppm): 100.4, −143.0 (septet, $^2J_{PF} = 707.6$ Hz). MALDI-TOF MS (*m*/*z*): 1789.0 (1790.1 for $[Cu_8(D)\{S_2P(O^iPr)_2\}_6]^+$), 892.73 $[Cu_8\{S_2P(O^iPr)_2\}_6]^{2+}$.

$[Cu_8\{S_2P(OEt)_2\}_6](PF_6)_2$, 3. The synthetic process is similar to that for **1**, though $NH_4[S_2P(OEt)_2]$ is used instead of $NH_4[S_2P(O^iPr)_2]$. Yield: 0.231 g (83%). Mp: 165 °C. Anal. calcd for $Cu_8H_{60}C_{24}O_{12}P_8F_{12}S_{12}$: C, 15.09; H, 3.17. Found: C, 15.30; H, 3.56%. ^1H NMR (acetone-d_6, δ, ppm): 1.39 (t, $^3J_{HH} = 7$ Hz, 36H, CH_3), 4.39 (m, 24H, OCH_2). ^{31}P NMR (acetone-d_6, δ, ppm): 93.9, −143.1 (septet, $^2J_{PF} = 708.0$ Hz). MALDI-TOF MS (*m*/*z*): 808.9 (809.9 for $[Cu_8\{S_2P(OEt)_2\}_6]^{2+}$).

$[Cu_4(\mu_4\text{-}H)(\mu_3\text{-}Cu)_4\{S_2P(OEt)_2\}_6](PF_6)$, 4a. $Cu(MeCN)_4PF_6$ (0.477 g, 1.28 mmol), $NH_4[S_2P(OEt)_2]$ (0.195 g, 0.96 mmol), and $NaBH_4$ (0.006 g, 0.16 mmol) were charged in a 100 mL Schlenk flask. A total of 30 mL of THF was added to it and was stirred at room temperature for 30 min. The reaction mixture was filtered, and the filtrate was evaporated to dryness under a vacuum to obtain a brown solid. The solid was washed with deionized water and dried under a vacuum to get $[Cu_4(\mu_4\text{-}H)(\mu_3\text{-}Cu)_4\{S_2P(OEt)_2\}_6](PF_6)$ as a brown powder. Yield: 0.231 g (82%). Mp: 173 °C. Anal. calcd for $Cu_8H_{61}C_{24}O_{12}P_7F_6S_{12}\cdot 0.5C_4H_8O$: C, 17.33; H, 3.64. Found: C, 17.06; H, 3.86%. ^1H NMR (acetone-d_6, δ, ppm): 1.39 (t, $^3J_{HH} = 7.0$ Hz, 36 H, CH_3), 3.49 (bs, 1H, μ_4-H), 4.27 (m, 24H, OCH_2). ^{31}P NMR (acetone-d_6, δ, ppm): 104.6, −143.1 (septet, $^2J_{PF} = 707.6$ Hz). MALDI-TOF MS (*m*/*z*): 1619.9 (1620.7 for $[Cu_8(H)\{S_2P(OEt)_2\}_6]^+$).

$[Cu_4(\mu_4\text{-}D)(\mu_3\text{-}Cu)_4\{S_2P(OEt)_2\}_6](PF_6)$, 4b. Compound **4b** was prepared in a similar fashion to **2a** by using $NaBD_4$. Yield: 220 g (78%). Mp: 175 °C. Anal. calcd for $Cu_8H_{60}DC_{24}O_{12}P_7F_6S_{12}$: C, 16.32; H, 3.54. Found: C, 16.00; H, 3.65%. ^1H NMR (acetone-d_6, δ, ppm): 1.39 (t, $^3J_{HH} = 7.0$ Hz, 3H, CH_3), 4.26 (m, 2H, OCH_2). ^2H NMR (acetone-d_6, δ, ppm): 3.47 (bs, 1D). ^{31}P NMR (acetone-d_6, δ, ppm): 104.6, −143.1 (septet, $^2J_{PF} = 707.5$ Hz). MALDI-TOF MS (*m*/*z*): 1620.9 (1621.7 for $[Cu_8(D)\{S_2P(OEt)_2\}_6]^+$), 808.9 ($[Cu_8\{S_2P(OEt)_2\}_6]^{2+}$).

Mass Spectrometry. MALDI-TOF spectra were acquired using an Autoflex time-of-flight mass spectrometer (Bruker Daltonic, Bremen, Germany) equipped with a 337 nm nitrogen laser (10 Hz, 3 ns pulse width). Spectral data were obtained in the reflection mode with an acceleration voltage of 20 kV. Each mass spectrum was derived from 100 summed scans. 2,5-Dihydroxybenzoic acid was used as a MALDI matrix, which was prepared by dissolving DHB in a solvent mixture of 50% MeOH and 0.1% TFA at a concentration of ca. 50 mM. An aliquot of the sample solution (0.5 μL) was mixed with an equal volume of the matrix solution and then applied on the target plate and dried before MALDI-TOF MS analysis. The theoretical isotopic distribution pattern was obtained by using Bruker Daltonic Isotope Pattern Anwendung software.

Crystal Structure Determination Procedure. Single crystals suitable for X-ray crystallography for **2a** were obtained by diffusing hexane into an acetone solution of the compound, and **4a** was obtained by diffusing benzene into an acetone solution of the compound. They were mounted on the tip of glass fibers with epoxy resin, and the data were collected on an APEX II CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073Å). Data reduction was performed with *SAINT*,[20] which corrects for Lorentz and polarization effects. A multiscan absorption correction based on SADABS was applied. Structures were solved by the use of direct methods, and the refinements were performed by the least-squares methods on F^2 with the SHELXL-97 package,[21] incorporated in SHELXTL/PC V5.10.[22] All Cu atoms in **2a** were disordered in two positions with equal probability. Eight Cu atoms in **4a** were also disordered in two orientations with the major component in 55% occupancy. One of the isopropyl groups (C16−C18) in **2a** was heavily disordered. It is separated into two parts with equal probability, as was the PF_6^- anion. H atoms on the alkyl side chains were placed at idealized positions. The central H^- for **2a** was placed at the inversion center, and its isotropic displacement parameter (Uiso) was fixed to 0.04. In compound **4a**, the central H^- was uncovered from the difference Fourier map, and its position was refined. However, its Uiso could not be refined (unreasonably small) and was, hence, fixed to 0.04. The crystallographic data are presented in Table 1, with selected bond distances and angles in Table 2.

Results and Discussion

Reaction of $NH_4[S_2P(OR)_2]$ (R = ^{i}Pr, **i**; Et = **ii**) with $[Cu(MeCN)_4]PF_6$ in acetone in a 6:8 molar ratio at room temperature for an hour results in copper clusters with the formula $[Cu_8\{S_2P(OR)_2\}_6](PF_6)_2$ (R= ^{i}Pr, **1**; Et, **3**) (eq 1).

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Table 1. Crystallographic Data for **2a** and **4a**·$0.5C_6H_6$

	2a	**4a**·$0.5C_6H_6$
formula	$C_{36}H_{85}Cu_8F_6O_{12}P_7S_{12}$	$C_{27}H_{64}Cu_8F_6O_{12}P_7S_{12}$
fw	1933.87	1804.61
cryst symmetry	monoclinic	trigonal
space group	$C2/c$	$R\bar{3}c$
a, Å	23.9657(9)	17.3818(16)
b, Å	12.7661(4)	17.3818(16)
c, Å	24.4885(8)	71.534(7)
α, deg	90	90
β, deg	91.2250(10)	90
γ, deg	90	120
V, Å^3	7490.5(4)	18717(3)
Z	4	12
T, K	296(2)	296(2)
ρ_{calcd}, g/cm^3	1.715	1.921
μ, mm^{-1}	2.769	3.317
reflns collected	28493	22580
independent reflns	9328 ($R_{int} = 0.0391$)	5176 ($R_{int} = 0.0607$)
data/restraints/params	9328/0/456	5176/ 0/237
Final R indices [$I > 2\sigma(I)^{a,b}$]	$R1 = 0.0550$ $wR2 = 0.1368$	$R1 = 0.0605$ $wR2 = 0.1410$
R indices (all data)	$R1 = 0.0924$ $wR2 = 0.1596$	$R1 = 0.1221$ $wR2 = 0.1738$
GOF	1.032	1.084
$\Delta\rho_{max}$, e Å^{-3}	1.678	1.135
$\Delta\rho_{min}$, e Å^{-3}	−0.864	−1.154

[a] $R1 = \sum |F_o| - |F_c|/\sum |F_o|$. [b] $wR2 = \{\sum [w(F_o^2 - F_c^2)^2]/\sum [w(F_o^2)^2]\}^{1/2}$.

On the other hand, the reaction of $NH_4[S_2P(OR)_2]$ with $[Cu(MeCN)_4]PF_6$ in the presence of $NaBH_4$ in a 6:8:1 molar ratio in THF at room temperature for 30 min gives rise to clusters with the formula $[Cu_4(H)(\mu_3\text{-}Cu)_4\{S_2P(OR)_2\}_6](PF_6)$ [R = ^{i}Pr, **2a**; Et, **4a**] (eq 2). Similar reactions carried out in the presence of $NaBD_4$ instead of $NaBH_4$ produce $[Cu_4(D)(\mu_3\text{-}Cu)_4\{S_2P(OR)_2\}_6](PF_6)$ [R = ^{i}Pr, **2b**; Et, **4b**] (eq 3). The reaction mixture was filtered to get rid of any solids formed, and the filtrate was evaporated under a vacuum to obtain the complexes. Afterward, the compounds were washed with copious amounts of water to get rid of NH_4PF_6. All of the compounds were characterized by ^{1}H NMR, ^{31}P NMR, microanalysis data, and MALDI-TOF mass spectrometry. Compounds **2b** and **4b** were further characterized using ^{2}H NMR spectra. In addition, structural elucidations of **2a** and **4a** were determined by single-crystal X-ray crystallography.

$$6NH_4[S_2P(OR)_2]\ (R = {}^i\text{Pr}, \mathbf{i};\ \text{Et}, \mathbf{ii}) + 8[Cu(MeCN)_4]PF_6 \rightarrow [Cu_8\{S_2P(OR)_2\}_6](PF_6)_2\ (R = {}^i\text{Pr}, \mathbf{1};\ \text{Et}, \mathbf{3}) + 6NH_4PF_6 + 32MeCN \quad (1)$$

$$6NH_4[S_2P(OR)_2]\ (R = {}^i\text{Pr}, \mathbf{i};\ \text{Et}, \mathbf{ii}) + 8[Cu(MeCN)_4]PF_6 + NaBH_4 \rightarrow [Cu_4(H)(\mu_3\text{-}Cu)_4\{S_2P(OR)_2\}_6](PF_6)\ (R = {}^i\text{Pr}, \mathbf{2a};\ \text{Et}, \mathbf{4a}) + NaPF_6 + 6NH_4PF_6 + 0.5(B_2H_6) + 32MeCN \quad (2)$$

$$6NH_4[S_2P(OR)_2]\ (R = {}^i\text{Pr}, \mathbf{i};\ \text{Et}, \mathbf{ii}) + 8[Cu(MeCN)_4]PF_6 + NaBD_4 \rightarrow [Cu_4(D)(\mu_3\text{-}Cu)_4\{S_2P(OR)_2\}_6](PF_6)\ (R = {}^i\text{Pr}, \mathbf{2b};\ \text{Et}, \mathbf{4b}) + NaPF_6 + 6NH_4PF_6 + 0.5(B_2D_6) + 32MeCN \quad (3)$$

Crystallography. Complex 2a. The monocationic, octanuclear copper cluster (Figure 1a) crystallizes in the monoclinic space group $C2/c$, which contains a tetracapped tetrahedral copper core surrounded by six diisopropyl dithiophosphate ligands along with an interstitial hydride anion and the counteranion PF_6^-. In crystallography, 16 copper atoms, each in 50% occupancy, form two cubes with one inside the other (Scheme 1). Thus, only four copper atoms in each cube are fully occupied. The reason that the geometry of the Cu_8 cluster is modeled as the tetracapped tetrahedron is due to the symmetry which required the simultaneous satisfaction of both C_2 and C_3 rotational axes to have all six dithiophosphate ligands equivalent magnetically in solution, as clearly evident from its ^{1}H and ^{31}P NMR spectra (vide infra). In the copper core, Cu5, Cu6, Cu7, and Cu8 (generalized as Cu_v) comprise the tetrahedron, whereas Cu1A, Cu2A, Cu3, and Cu4A (generalized as Cu_{cap}) are capped to the four triangular faces of the tetrahedron (Figure 1b). The Cu···Cu distances through the edges of the tetrahedron lie between 2.908(2) and 3.116(3) Å (Cu_v−Cu_v in Table 2). However, the distances between copper atoms at the vertex to the capping Cu atoms (Cu_v−Cu_{cap}) vary from 2.6759(17) to 2.7512(19) Å and are shorter than those of the Cu_v−Cu_v distances. All of the Cu−Cu distances are shorter than those identified in the empty-caged, octanuclear copper cluster $[Cu_8(S_2PPh_2)_6]^{2+}$ (3.1275(16)− 3.2861(14) Å).[6a] Cu_v−Cu_v distances (2.908(2)−3.116(3) Å) are longer than the sum of its van der Waal radii (2.8 Å); however, all of the Cu_{cap}−Cu_v distances lie below the cutoff limit mentioned above in the octanuclear cubic core. The hydride anion entrapped inside the copper cage shows interactions to four Cu_v atoms with distances ranging from a minimum of 1.7524(15) Å (Cu5−H) to a maximum of 1.906(2) Å (Cu8−H). The C_3 axis passes through a Cu_v, the central hydride, and the Cu_{cap} atom. It also contains three C_2 axes passing through two opposite P atoms such as P1 and P1A. Each of the eight copper atoms is trigonally connected to three S atoms from three $[S_2P(O^iPr)_2]^-$ ligands in a *facial* manner. Interestingly, the capping Cu atoms (Cu1A, Cu2A, Cu3, and Cu4A) are almost in the same plane as the three S atoms coordinated to them. For example, Cu1A is 0.085(1) Å out of the plane constituted by S2A, S4, and S6. Each of the six bridging dithiophosphate ligands caps the Cu_4 butterfly, where the hinge position is the edge of the tetrahedron and the wingtips are two capping Cu atoms. The dihedral angles of the Cu_4 butterflies lie between 153 and 155°. Thus, the 12 μ_2-S atoms out of six dithiophosphate ligands are arranged in a nearly icosahedron, and the coordination pattern of the dithiophosphate ligand is tetrametallic tetraconnective (μ_2-S; μ_2-S). The averaged, intraligand S···S bite distance is 3.469(2) Å. The Cu_v−S bond distances (2.3974(19)−2.4544(16) Å) are longer than those of Cu_{cap}−S (2.1841(16)−2.2441(16) Å). The Cu_{cap}−S distances are in the same range as those observed in the octanuclear cubic copper cluster $[Cu_8(S_2PPh_2)_6]^{2+}$ (2.228(2)− 2.245(2) Å).[6a] The P−S distances lie in the range 1.9993(18)−

Table 2. Selected Bond Lengths (Å) and Angles (deg) with Estimated Standard Deviations Listed in Parentheses

	2a	4a(i)	4a(ii)
Cu−H	1.7524(15), 1.8177(18), 1.876(2), 1.906(2),	1.74(3) 2.08(7)	1.72(7) 1.97(2)
Cu_v−Cu_v[a]	2.908(2), 2.936(2), 2.995(2), 3.003(3), 3.054(3), 3.116(3),	2.826(3) 3.128(4)	3.009(5) 3.233(4)
Cu_v−Cu_{cap}[b]	2.6759(17), 2.7133(17), 2.722(2) 2.7259(17), 2.7261(19), 2.729(2), 2.7373(19), 2.743(2), 2.7458(19), 2.7499(17), 2.7504(19), 2.7512(19),	2.692(2) 2.714(2) 2.746(2) 2.842(3)	2.646(3) 2.687(3) 2.755(3) 2.788(4)
Cu_v−S	2.3974(19), 2.4070(18), 2.4084(18), 2.4103(19), 2.4140(18), 2.4142(19), 2.4190(17), 2.4241(16), 2.4247(17), 2.4318(17), 2.4379(18), 2.4544(16)	2.372(2) 2.426(2) 2.460(2) 2.480(2)	2.359(3) 2.386(3) 2.413(3) 2.440(3)
Cu_{cap}−S	2.1841(16), 2.1959(16), 2.2050(17), 2.2128(17), 2.2175(17), 2.2199(17), 2.2223(16), 2.2256(15), 2.2268(17), 2.2334(16), 2.2338(16), 2.2441(16)	2.1924(18) 2.213(2) 2.223(2) 2.265(2)	2.173(2) 2.236(2) 2.240(2) 2.2513(15)
S···S (bite)	3.465(2), 3.468(2), 3.475(2),	3.459(2), 3.471(2)	
S−P	1.9993(18), 2.0062(16), 2.0104(16), 2.0159(16), 2.0165(15), 2.0225(17)	1.991(2), 2.009(2) 2.026(2)	
P−O	1.545(4), 1.550(4), 1.556(3), 1.569(4), 1.572(4), 1.604(5)	1.533(5), 1.559(6), 1.566(4), 1.572(4)	
S−P−S	118.90(7), 118.97(7), 119.54(7)	118.89(10), 119.40(9)	
O−P−O	107.2(3), 108.9(2),112.3(3)	102.2(4), 107.1(2)	
dihedral angles of the Cu_4 butterfly	153, 154, 155	151 155	156 158

[a] Cu_v = Cu atoms at the vertex of the tetrahedron. [b] Cu_{cap} = Cu atoms capped to the tetrahedron face.

2.0225(17) Å and are slightly shorter than those observed in $[Cu_8(S_2PPh_2)_6]^{2+}$ (2.046(2)−2.056(3) Å).[6a]

Complex 4a. The monocationic octanuclear Cu(I) complex involving an ethyl homologue of the dithiophosphate ligand crystallizes in trigonal space group $R\bar{3}c$ along with one-half of the solvated benzene molecule and the counteranion PF_6^-. Although it is isostructural with **2a**, the copper framework is, however, disordered in two orientations with the major component in 55% occupancy. Thus, two metallic frameworks of the compound **4a**, namely, **4a(i)** (Figure S1a, Supporting Information) and **4a(ii)** (Figure S1b, Supporting Information), with 55 and 45% occupancy are generated. The structure of **4a(i)** consists of a tetracapped tetrahedral copper core in which Cu2, Cu2A, Cu2B, and Cu4 atoms form a tetrahedron, whereas Cu1, Cu1A, Cu1B, and Cu3 are the capping atoms (Figure S1c, Supporting Information). All of the metric data are listed in Table 2. Two intraligand S···S bite distances (3.459(2) and 3.471(2) Å) are observed. Cu6, Cu6A, Cu6B, and Cu8 are situated at the vertex (Cu_v) of a tetrahedron, and their faces are capped by Cu5, Cu5A, Cu5B, and Cu7 atoms (Cu_{cap}) in the core of **4a(ii)** (Figure S1d, Supporting Information), iso-structural to **4a(i)**. The average Cu_v−Cu_v distance (3.121 Å) is larger, but the Cu_{cap}−Cu_v distance (av. 2.719Å) is shorter in **4a(ii)** than those observed in **4a(i)** (Cu_{cap}−Cu_v 2.7485 Å (av); Cu_v−Cu_v 2.977 Å (av)).

The hydride-centered copper cluster reported in $[Cu_6(H)(Cl)\{Me_3(NCH_2)_3\}_3]^+$ exhibits a Cu−H distance of 1.85(3) Å,[8] which is similar to that in our compounds (average 1.84 Å for **2a**, 1.91 Å for **4a(i)**, 1.85 Å for **4a(ii)**). The Cu−Cu distances in the octahedral structure varying from 2.4566(8) to 2.7049(8) Å are shorter than those in **2a** and **4a**. However, Cu−Cu distances in $[Cu_3(dcpm)_3(\mu_3\text{-}H)](Y_2)$ (where dcpm = bis(dicyclohexylphosphino)methane; Y = ClO_4^-, BF_4^-, PF_6^-, $CF_3SO_3^-$), 2.879(1) and 2.885(1) Å,[9] are comparable to the Cu_v−Cu_{cap} distances of our compounds. Nevertheless, these compounds displayed shorter (~1.67 Å) Cu−H distances.

Indeed, a metal cluster with a tetracapped tetrahedral M_8 core structure is rare. Fenske and his co-workers reported $[Ni_8Se_6(P^iPr_3)_4]$, which contained a Ni_4 tetrahedron, each of the four triangular faces being capped by a Ni atom in its core, but the authors claimed that it was a distorted, cubic Ni_8 core.[23] Recently, Adams et al. reported an $Os_4(CO)_{12}[Pd(P^tBu_3)]_4$ compound which contained a tetrahedral Os_4 core, and each triangular face was capped by a palladium moiety.[24] Thus, there is no example of a Cu_8 cluster being a tetracapped tetrahedron. Most of the Cu_8 clusters supported by dichalcogenophosph(in)ate ligands show a cubic metallic

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(23) Fenske, D.; Krautscheid, H.; Muller, M. *Angew. Chem., Int. Ed.* **1992**, *31*, 321–323.

(24) Adams, R. D.; Boswell, E. M.; Captain, B. *Organometallics* **2008**, *27*, 1169–1173.

(25) (a) Goeden, G. V.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1986**, *25*, 2484–2485. (b) Lemmen, T. H.; Folting, K.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1985**, *107*, 7774–7775.

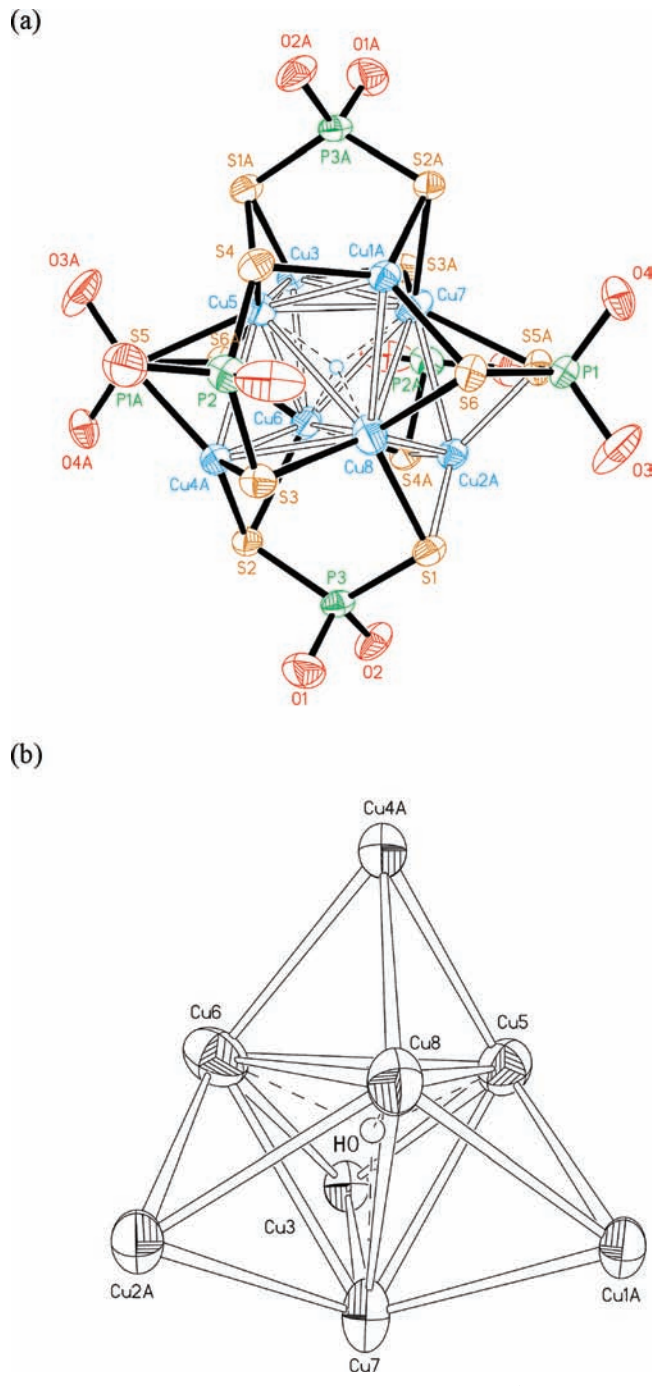
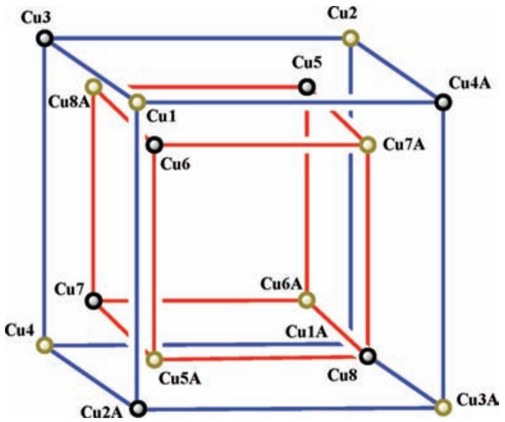


Figure 1. (a) Perspective view of $Cu_4(H)(\mu_3\text{-}Cu)_4[S_2P(O^iPr)_2]_6(PF_6)$, **2a**. Isopropyl groups have been omitted for clarity. (b) Cu_8 cage and the entrapped H atom in the cage in **2a**.

core.[5,6] The average Cu−(μ_8-X) distance in $[Cu_8\{S_2P(O^iPr)_2\}(\mu_8\text{-X})]^+$ was observed to be 2.72[6c] and 2.74 Å[6f] for Cl and Br, respectively. In comparison, compound **2a** shows an average Cu−H distance of 1.84 Å. Apparently, the encapsulation of the smallest closed-shell anion forced the cubic Cu_8 core to undergo a tetrahedral contraction due to the strong Cu−H interactions, as depicted in Scheme 2. Consequently, dissymmetric molecules of **2** and **4**, which display a hydride-centered tetracapped tetrahedral copper skeleton inscribed in a S_{12} icosahedral cage, have an idealized point group symmetry of *T*.

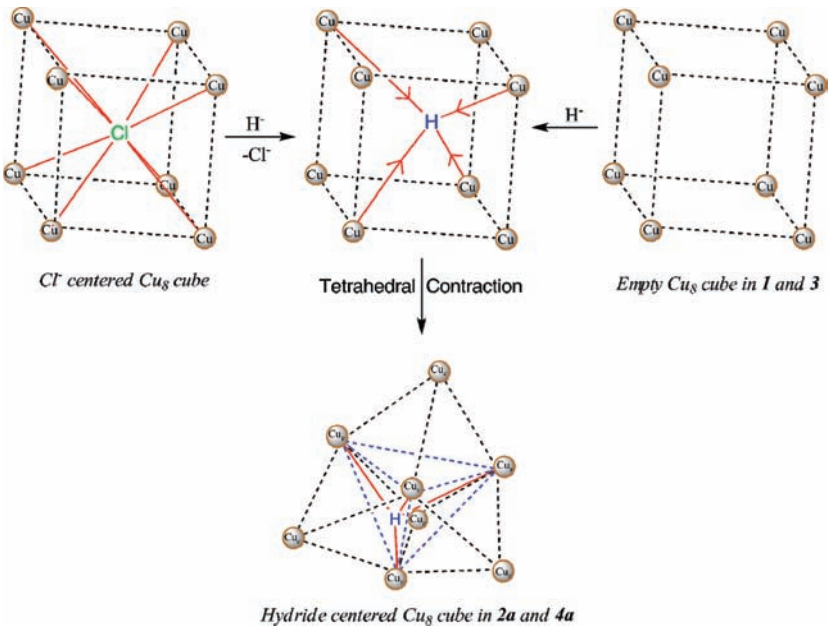
Scheme 1



NMR Spectroscopy. Compound **1** shows doublet (1.47 ppm) and multiplet (5.07 ppm) peaks for its methyl and methine protons, whereas compound **3** shows triplet (1.39 ppm) and multiplet (4.39 ppm) peaks for its methyl and methylene protons, respectively, in ^{1}H NMR spectra. Similarly, a ^{1}H NMR spectrum exhibits a doublet (1.42 ppm) and a multiplet (4.89 ppm) for **2a** from its methyl and methine protons (Figure 2a), while a triplet (1.39 ppm) and a multiplet (4.27 ppm) are exhibited for **4a** from its methyl and methylene protons. In addition, in the ^{1}H NMR spectrum, the hydride exhibits a broad singlet at 3.69 and 3.49 ppm for **2a** and **4a**, respectively. Presumably, the unresolved coupling of the hydride with copper nuclei ($I = 3/2$) results in peak broadening. A representative spectrum is given for compound **2a** in the figure inset. The integration ratio of the hydride and methine protons is 1:12 for **2a**. In a similar way, **2b** exhibits a doublet (1.43 ppm) and a multiplet (4.90 ppm) from its methyl and methine protons (Figure 2b), while **4b** exhibits a triplet (1.39 ppm) and a multiplet (4.26 ppm) from its methyl and methylene protons in the ^{1}H NMR spectrum. In addition, **2b** and **4b** show chemical shifts originated from their deuterium nuclei at 3.71 and 3.47 ppm in the ^{2}H NMR spectrum. The deuterium peak is also broad. A representative ^{2}H NMR spectrum of compound **2b** is shown in the inset of Figure 2b. Caulton et al. observed broad unstructured proton signals for the hydride coordinated to copper clusters, $Cu_2(\mu\text{-}H)_2\{MeC(CH_2PPh_2)_3\}_2]$,[25a] $[HCuP(NMe_2)_3]_6$, and $H_8Cu_8\text{-}[Ph_2P(CH_2)_3PPh_2]_4$,[25b] in ^{1}H NMR and ^{2}H NMR (after deuterium exchange) spectra which are reminiscent of our NMR results, a broad singlet for the hydride and deuteride resonance. No hydride resonance was reported in $[Cu_6(H)(Cl)\{Me_3(NCH_2)_3\}_3]^+$.[8]

^{31}P NMR spectra of all of the compounds display a resonance for the P atom of the hexafluorophosphate counteranion at ~143 ppm with $J_{PF} = 708$ Hz. ^{31}P NMR spectra of compounds **1** and **3** exhibit singlet peaks at 88.8 and 93.9 ppm, respectively, originated from the P atom of the ligands. On the other hand, both **2a** and **2b** show a singlet at 100.4 ppm, while both **4a** and **4b** show a singlet at 104.6 ppm in the ^{31}P NMR spectrum. Thus, both the hydride and deuteride entrapped complexes exhibit a downfield shift compared to the empty Cu_8 clusters. All of these NMR data suggest that all six ligand units present in each of the compounds remain

Scheme 2



in a similar chemical environment in solution. It is noted that $[Cu_8(Cl)\{S_2P(O^iPr)_2\}_6]^+$ and $[Cu_8(Br)\{S_2P(O^iPr)_2\}_6]^+$ resonate at 90.2 and 92.3 ppm, respectively, in the ^{31}P NMR spectrum.[6f]

Mass Spectrometry. The positive MALDI-TOF mass spectra of the hydride- and deuteride-encapsulated compounds **2a**,**b** display the molecular ion peak for the cations $[Cu_8(X)L_6]^+$ ($X = H$ or D, $L = [S_2P(O^iPr)_2]$) with a (-1) isotopic shift, which is consistent for all of the compounds. A representative picture (Figure 3a) shows the spectrum of compound **2a**. The molecular ion peak is magnified and presented in the inset of Figure 3a along with the theoretical isotopic distribution for comparison. In Figure 3b, a deuterium entrapped molecule, **2b**, shows the molecular ion peak, just 1 amu higher than that for compound **2a**. The inset shows the isotopic distribution of the molecular ion peak obtained both experimentally and theoretically. The experimentally obtained isotopic distribution peaks are very similar to theoretical values, as evident from the figure. Both **2a** and **2b** show a fragment peak at ~893 with 100% intensity corresponding to $[Cu_8L_6]^{2+}$. Compound **1** also displays a peak at 892.8 for the dicationic species $[Cu_8L_6]^{2+}$ instead of showing peaks for monocationic $[(Cu_8L_6)(PF_6)]^+$ or molecular $[Cu_8L_6](PF_6)_2$ species. A similar pattern is observed for the ethyl homologue **4a**,**b** which displays peaks corresponding to monocationic species $[Cu_8(X)L_6]^+$ ($X = H$ or D, $L = [S_2P(OEt)_2]$) at 1619.9 and 1620.9, respectively, along with dicationic species $[Cu_8L_6]^{2+}$ at ~809 with 100% intensity. Thus, the peak observed for **3** at *m/z* 808.85 could undoubtedly originate from the dicationic species $[Cu_8\{S_2P(OEt)_2\}_6]^{2+}$.

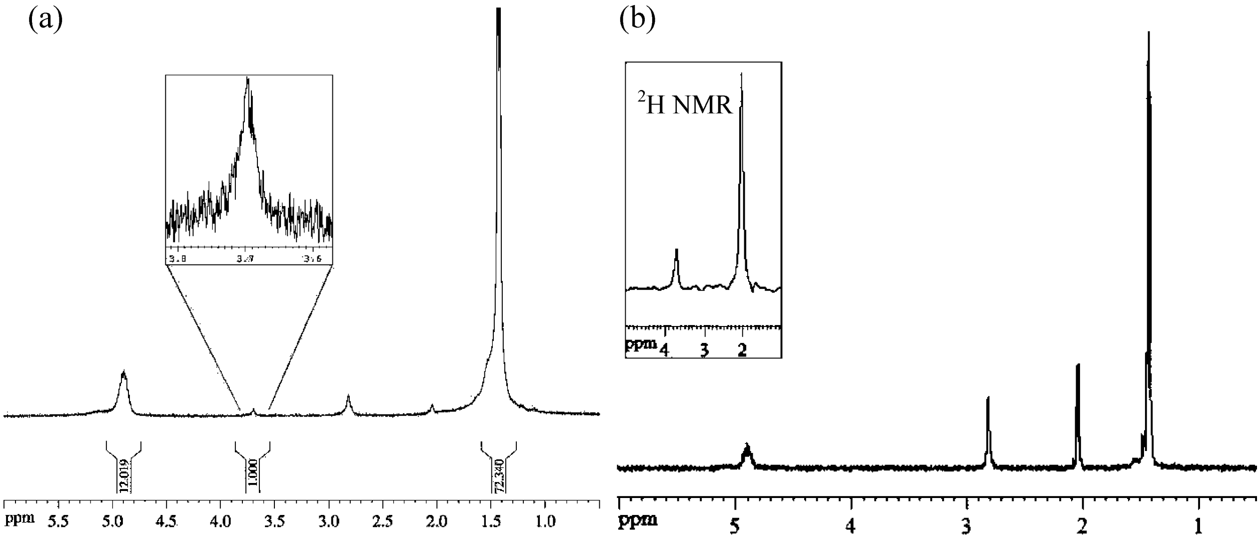


Figure 2. (a) ^1H NMR spectrum of $[Cu_4(H)(\mu_3\text{-}Cu)_4\{S_2P(O^iPr)_2\}_6](PF_6)$, **2a**, at RT. The peaks at 2.04 and 2.82 are originated from acetone and water protons. Inset: The peak at 3.69 is magnified. (b) ^1H NMR spectrum of $[Cu_4(D)(\mu_3\text{-}Cu)_4\{S_2P(O^iPr)_2\}_6](PF_6)$, **2b**, at RT. The peaks at 2.04 and 2.82 arise from acetone and water protons. Inset: ^2H NMR spectrum of $[Cu_4(D)(\mu_3\text{-}Cu)_4\{S_2P(O^iPr)_2\}_6](PF_6)$, **2b**. The peak at 2.04 is from acetone.

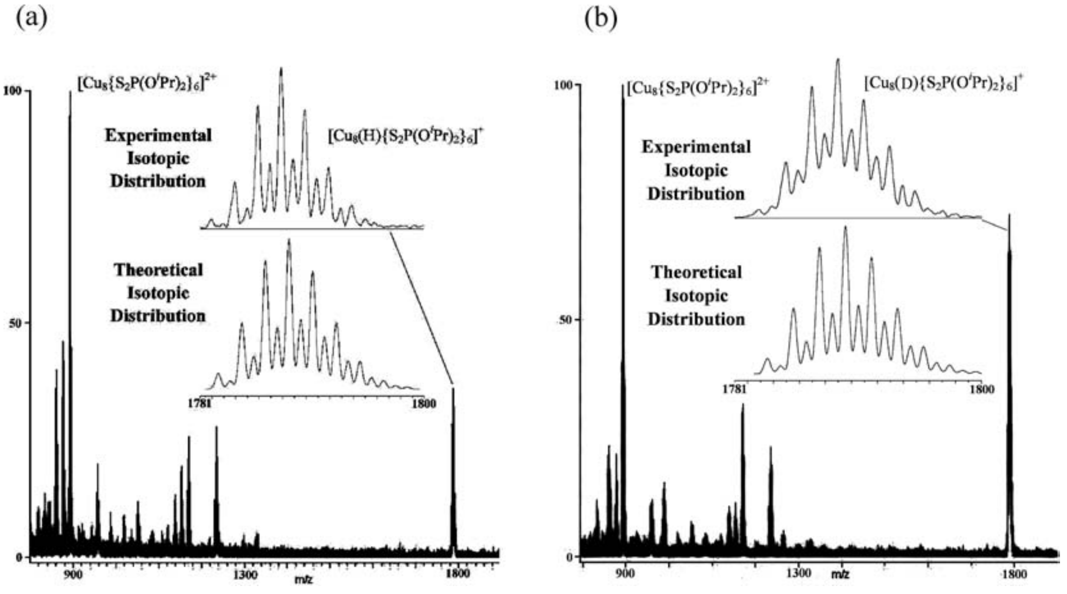
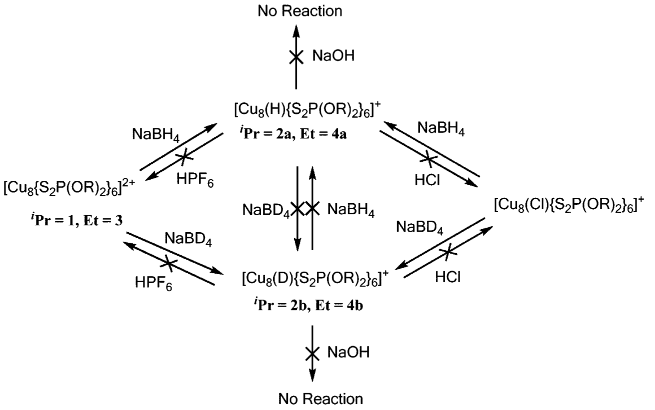


Figure 3. Representative positive MALDI-TOF mass spectra of (a) **2a** and (b) **2b**.

Scheme 3



Reactivity of the Complexes. In 2008, Davies et al. reported the structure of dicationic $[Cu_8(S_2PPh_2)_6]^{2+}$, which contains an empty Cu^I_8 cubic cage coordinated by six dithiophosphinate ligands from each face of the cube in μ_4 fashion.[6a] Keep in mind the very similar structure of dithiophosphate ligands $[S_2P(OR)_2]^-$ and the similar μ_4-coordinating pattern of the ligands in compounds **2a** and **4a**, we assume the existence of a Cu_8 empty core in compounds **1** and **3**. Unfortunately, good-quality single crystals could not be isolated to perform detailed X-ray diffraction studies, but the hydride (or deuteride) encapsulated compounds (**2** and **4**) can also be derived by adding 1 equiv of $NaBH_4$ or $NaBD_4$ to the empty, octanuclear copper complexes (**1** and **3**), which were confirmed by ^{31}P, ^{1}H, and ^{2}H NMR spectroscopy (Scheme 3). For example, when $NaBH_4$ is added to **1**, after workup, the broad peak at 3.69 ppm appeared in the ^{1}H NMR and ^{31}P NMR spectra shows a ~12 ppm downfield shift for the ligand phosphorus. The progress of the reaction can be followed by the ^{31}P NMR experiment. After the ^{31}P NMR of **1** was measured, 1 equiv of $NaBH_4$ was added to the same NMR tube. Measurements at 30 s intervals were then started, and each spectrum was collected after 10 scans, having a delay time of 3 s. The spectra show two peaks at 88.8 and 100.4 ppm after 3 min, whereas the new peak corresponds to the resonance of $[Cu_8(H)\{S_2P(O^iPr)_2\}_6]^+$ (**2a**; Figure 4). The reaction was complete within ~30 min without any detectable intermediates. This suggests the accessibility of the empty Cu_8 core by the added anion through opening up of the cluster core either by breakage then reformation or by distortion of the central, cubic portion. Presumably, the driving force is the geometry change of the Cu_8 core from cube to tetracapped tetrahedron in the presence of an interstitial hydride. Assuming the peak integration in the ^{31}P NMR spectrum is equivalent to the concentration of the reactants, the log of the peak integration versus time (Figure S2, Supporting Information) is plotted to understand the probable reaction kinetics. Unfortunately, the complicated nature of the plot suggests that the reaction was neither a simple zeroth nor first-order reaction. So we assume that the hydride insertion reaction may proceed through the formation of some transient intermediates in solution by either the partial breakage or distortion of the parent complex. Similarly, when $NaBD_4$ is added to **1**, the ^{31}P NMR spectrum shows a ~12 ppm downfield shift, while the ^{2}H NMR spectrum shows the appearance of a broad singlet at 3.71 ppm. Furthermore, these robust hydride- or deuteride-centered compounds **2** and **4** could be generated even if an excess amount of $NaBH_4$ or $NaBD_4$ was used in the synthesis.

Upon the addition of $NaBH_4/NaBD_4$ to the Cl^- encapsulated complex $[Cu_8(Cl)\{S_2P(OEt)_2\}_6](PF_6)$, the encapsulated chloride can be replaced by the hydride or deuteride, which is certified by ^{31}P NMR spectroscopy (Scheme 3). After the addition of $NaBH_4$ to the NMR tube containing $[Cu_8(\mu_8\text{-}Cl)\{S_2P(OEt)_2\}_6]^+$, which resonates at 98.4 ppm in THF, ^{31}P NMR spectra were measured. The spectra show two peaks at 98.4 and 104.2 ppm after 5 min, whereas the new peak corresponds to the $[Cu_8(H)\{S_2P(OEt)_2\}_6]^+$ (**4a**; Figure S3, Supporting Information). The reaction was complete within

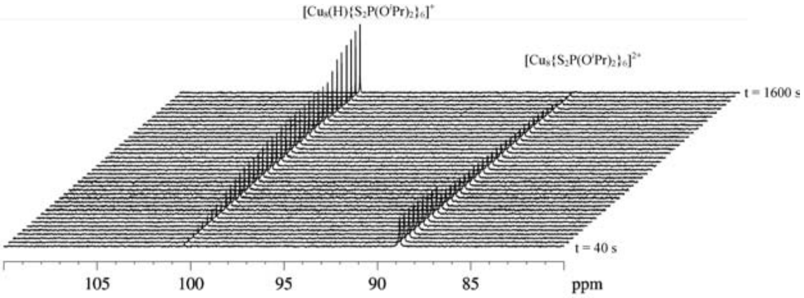


Figure 4. Progress of the reaction from $[Cu_8\{S_2P(O^iPr)_2\}_6]^{2+}$ to $[Cu_8(H)\{S_2P(O^iPr)_2\}_6]^+$ in the presence of $NaBH_4$ certified by ^{31}P NMR spectroscopy.

~30 min, as evident from the final ^{31}P NMR spectrum, which contains a single peak at 104.2 ppm. The driving force for the replacement reaction is the change of the geometry of the Cu_8 core from cubic to tetracapped tetrahedral (Scheme 2).

Molecules concentric with a chloride-centered cubic Cu^I skeleton surrounded by 12 sulfur atoms in a distorted icosahedral cage are believed to be the most stable species in the series of anion-centered cubic copper clusters.[5a,6a,b,e,26] This characteristic is further demonstrated in the mixed-valence cluster of $Cu^I_8Cu^{II}_6(Cl)(D\text{-}Pen)_{12}^{5-}$ [1] and extended to the selenium-donor ligands.[6b,c] Unfortunately, the replacement reaction of chloride by hydride is not reversible. Otherwise, this reaction may provide an alternative way to regenerate the dithiophosphate copper species, which are key ingredients of the antioxidants in lubricant oils.[27]

It is known that the molecular H_2 can be produced from transitional metal hydrides upon protonation.[28] Surprisingly, the hydride/deuteride could not be replaced from either **2** and **4** by adding HPF_6 or HCl. Treatment of **2** and **4** with an acid or base for prolonged stirring simply decomposes the complex followed by the decomposition of the ligand units (Scheme 3). It seems that the complexes with the tetracapped tetrahedral geometry of Cu_8 are more stable than the cubic orientation observed in $[Cu_8(X)\{S_2P(OR)_2\}_6]^+$. It is not surprising that the smaller hydride sneaked into the larger cavity of the chloride-containing compounds, and then the consequent geometry change does not allow the larger halide anions to sneak back inside the small cavity. Thus, we want to see if the hydride could be exchanged by the deuteride, which has a similar size, and vice verse. The addition of $NaBD_4$ to **2a** and **4a** did not produce any peak in ^2H NMR for the encapsulated deuteride. Similarly, the addition of $NaBH_4$ to **2b** and **4b** also did not produce any peak at ~3.69 ppm in the ^1H NMR spectrum for the encapsulated hydride by the hydride-deuteride exchange (Scheme 3).

In conclusion, we have demonstrated the synthesis and structural elucidation of the hydride-encapsulated Cu_8 clusters, which are supported by six dithiophosphates and have a tetracapped-tetrahedral copper core. This geometry is in sharp contrast to most of the cubic Cu_8 clusters supported by dichalcogenophosph(in)ate ligands. This geometry, being very much unusual, is formed by tetrahedral contraction of the cubic copper core due to the interactions with the interstitial hydride, the smallest closed-shell anion. Also, we have demonstrated the higher stability of this type of structure, which is confirmed by the facile replacement of chloride from $[Cu_8(Cl)L_6]^{2+}$ with H^- to form the hydride-centered clusters, but the reverse reaction was unsuccessful. Although the mechanism is not clear, it is well confirmed that the empty Cu_8 cubic core is accessible in **1** and **3** by anions, and that the flexibility of the tetrametallic tetraconnective binding pattern of the dithiophosphate ligand allowed the cubic metallic core to undergo distortion, forming the tetracapped-tetrahedral geometry. Preliminary studies indicate that hydride-centered tetracapped tetrahedral copper clusters can be used as efficient procatalysts for the Ulmann-type coupling reactions, and the synthesis can be extended to the dithiocarbamate-type ligands. The results will be forthcoming.

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Supporting Information Available: X-ray crystallographic files in CIF format for compounds **2a** and **4a** and Figures S1−S3. This material is available free of charge via the Internet at http://pubs.acs.org.

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