

Characterization and Reactions of $[\text{PPh}_4]_3[\text{Zr}_6\text{Cl}_{18}\text{H}_5]$ and Its Deprotonation Products

Lin Feng Chen,^{1a} F. Albert Cotton,^{*,1a} Wim T. Klooster,^{1b} and Thomas F. Koetzle^{1b}

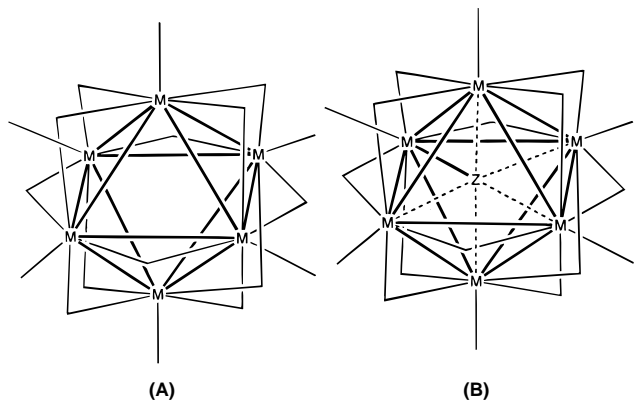
Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843, and Chemistry Department, Brookhaven National Laboratory, P.O. Box 5000, Upton, New York 11973-5000

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Abstract: The octahedral hexazirconium cluster compound $[\text{PPh}_4]_3[\text{Zr}_6\text{Cl}_{18}\text{H}_5]$ has been structurally characterized by both neutron and X-ray single-crystal diffraction studies. The compound $[\text{PPh}_4]_3[\text{Zr}_6\text{Cl}_{18}\text{H}_5] \cdot 3\text{CH}_2\text{Cl}_2$ crystallizes in the triclinic space group $P\bar{1}$ with unit cell parameters of $a = 15.993(3)$, $b = 22.237(3)$, and $c = 14.670(4)$ Å, $\alpha = 95.31(1)$, $\beta = 112.07(2)$, and $\gamma = 82.06(2)^\circ$, $V = 4784(2)$ Å³, and $Z = 2$ at ambient temperature and $a = 15.780(6)$, $b = 21.96(3)$, and $c = 14.521(7)$ Å, $\alpha = 94.96(8)$, $\beta = 111.59(4)$, and $\gamma = 81.72(5)^\circ$, $V = 4627(11)$ Å³, and $Z = 2$ at $T = 15$ K. The hydrogen atoms in the cluster anion, $[\text{Zr}_6\text{Cl}_{18}\text{H}_5]^{3-}$, were found to be distributed at the centers of the eight triangular faces of the Zr_6 octahedron from neutron diffraction data. The occupancy parameters of the sites range from 0.32 to 0.92 with a total of 5.3(1) hydrogen atoms per cluster, close to the value from ¹H NMR measurement (5.0). The average Zr–H distance is 1.96(4) Å. A variable temperature ¹H NMR study indicated that the cluster hydrogen atoms undergo rapid movement at room temperature. One of the five hydrogen atoms in the cluster $[\text{Zr}_6\text{Cl}_{18}\text{H}_5]^{3-}$ was readily removed as a proton with primary linear amines with formation of the corresponding ammonium cations, while the cluster anion, $[\text{Zr}_6\text{Cl}_{18}\text{H}_5]^{3-}$, was thus converted into a new cluster anion, $[\text{Zr}_6\text{Cl}_{18}\text{H}_4]^{4-}$. The feasibility of such a deprotonation reactions is controlled by the size of both the Lewis base and the cavity available on the Zr_3 triangular faces of the Zr_6 clusters, and also by the basicity of the deprotonating reagents. Two products, $[\text{PPh}_4]_4[\text{Zr}_6\text{Cl}_{18}\text{H}_4] \cdot 4\text{CH}_2\text{Cl}_2$ and $[\text{H}_3\text{NEt}]_4[\text{Zr}_6\text{Cl}_{18}\text{H}_4] \cdot 4\text{MeCN}$ from the deprotonation reactions were characterized by X-ray crystallography.

Introduction

Many halide-supported hexanuclear transition metal clusters adopt the octahedral structure (A) with halides bridging the 12 edges of the cluster.^{2a–f} These clusters usually require 14 or 16 valence electrons to achieve a stable closed shell configuration. When the metal atoms are electron deficient, for example, for the early transition metals, the cluster may incorporate a foreign atom into the cluster as an interstitial atom (B) of which the electrons are used to meet the electronic requirement.



A series of hexazirconium clusters of the $\text{Zr}_6\text{X}_{12}\text{Z}$ ($\text{X} = \text{Cl}, \text{Br}, \text{and I}$) type from solid state reactions have been extensively studied by Corbett and coworkers.^{3a–c} These clusters can be synthesized in high yields by purposely including the interstitial atom source in the reactions. Clusters are known with interstitial atoms, Z, including both nonmetal (*e.g.*, Be, B, C, N, Si, Ge, and P) and metal elements (*e.g.*, K, Al, Cr, Mn, Fe, Co, and Ni). Not surprisingly, all of these centered clusters have the type B structure. The cluster units, $\text{Zr}_6\text{X}_{12}\text{Z}$, are often connected to each other by sharing the halogen atoms. The interstitial atoms were located from X-ray diffraction studies. A 14-electron configuration is preferred for these clusters with main group interstitial atoms.

There is evidence that one or more hydrogen atoms may also be incorporated into the hexazirconium clusters. $[\text{Zr}_6\text{Cl}_{12}\text{H}]^4$ and $\text{Li}_6[\text{Zr}_6\text{Cl}_{18}\text{H}]^5$ have both been obtained from solid state synthesis. Displacement of chloride ions in $\text{Li}_6[\text{Zr}_6\text{Cl}_{18}\text{H}]$ by EtNH_2 ligands resulted in the formation of a new cluster, $[\text{Zr}_6\text{Cl}_{12}\text{H}(\text{EtNH}_2)_6]$,⁶ which was also assumed to contain a hydrogen atom. Because of the limitation of X-ray diffraction, the hydrogen atoms were not located in these three compounds. Due to its uniquely small core size and high mobility, the hydrogen atom may differ from other interstitial atoms. Not much has been known about the behavior of hydrogen atoms in octahedral hexanuclear clusters.^{7,8} For early transition metals besides zirconium, only one hydrogen-containing cluster, namely,

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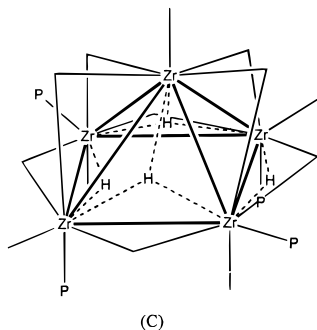
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$\text{Th}_6\text{Br}_{15}\text{H}_7$, has been well characterized.^{8b} This compound was also prepared from a solid state reaction and has been structurally characterized by neutron diffraction.^{8b}

In an effort to characterize the hydrogen atom, $\text{Li}_6[\text{Zr}_6\text{Cl}_{18}\text{H}]$ was studied by inelastic neutron scattering, and the observations were rationalized in terms of a model with the hydrogen atom occupying a μ_3 -bridging position within the Zr_6 octahedron with a Zr–H bond distance of ca. 2.0 Å.⁹ $[\text{Zr}_6\text{Cl}_{12}\text{H}]$ was studied by solid state ^1H NMR.¹⁰ The results indicate that the hydrogen atom undergoes random motion on the NMR time scale, in accord with the oversized Zr_6 metal cluster cavity available. However, the number and position(s) of the cluster hydrogen atom(s) have never been unambiguously determined.

By reducing ZrX_4 ($X = \text{Cl}, \text{Br}$) with HSnBu_3 , we have developed an alternative way to prepare zirconium clusters containing hydrogen atoms under mild conditions (room temperature in organic solvents).^{11–21} A series of pentanuclear clusters ($[\text{Zr}_5\text{Cl}_{12}(\text{PR}_3)_5\text{H}_4]$)¹⁴ and hexanuclear clusters ($[\text{Zr}_6\text{Cl}_{18}\text{H}_5]^{3-}$),¹⁷ $[\text{Zr}_6\text{Cl}_{18}\text{H}_4]^{4-}$,¹⁸ $[\text{Zr}_6\text{Cl}_{18}\text{H}_5]^{2-}$,¹⁹ $[\text{Zr}_6\text{Cl}_{14}(\text{PR}_3)_4\text{H}_4]$,¹⁶ $[\text{Zr}_6\text{Cl}_{12}(\text{PMe}_2\text{Ph})_6\text{H}_2]$,^{13,20} $[\text{Zr}_6\text{Cl}_{12}(\text{PEt}_3)_6\text{H}_3]^+$,²⁰ and $[\text{Zr}_6\text{Cl}_{13}(\text{PEt}_3)_5\text{H}_3]^{20}$ have been synthesized by this new method. From a deuterium labeling experiment, the cluster hydrogen atoms were proved to come from the tin hydride reducing reagent HSnBu_3 .¹⁷ The four hydrogen atoms in the pentanuclear cluster $[\text{Zr}_5\text{Cl}_{12}(\text{PR}_3)_5\text{H}_4]$ were located from an X-ray diffraction study, with two of them μ_3 -bridging two opposite Zr_3 faces and the other two μ_2 -bridging two opposite Zr_2 units (C).¹⁵ For each



of the hexanuclear clusters, the number of cluster hydrogen

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atoms was determined from ^1H NMR studies by integrating the signal of cluster hydrogen atoms against the proton signals of the counterions.^{15,20} From X-ray crystallographic studies, residual electron densities were found close to the centers of the eight triangular faces of the Zr_6 octahedron; they can be refined as partial hydrogen atoms when the X-ray diffraction data set is good. It appeared that the hydrogen atoms in the hexanuclear clusters are disordered or distributed on the eight Zr_3 faces. However, because X-ray diffraction is not a very reliable and convincing method to locate hydrogen atoms, especially in the Zr_6 clusters accompanied by disorder, a neutron structure was felt to be needed to support and verify the results from X-ray diffraction.

A structure based on neutron diffraction data has been obtained from a crystal of $[\text{PPh}_4]_3[\text{Zr}_6\text{Cl}_{18}\text{H}_5]$.²¹ Although the five hydrogen atoms in this structure were indeed found to be distributed at the centers of the eight Zr_3 faces (in accord with the results from X-ray crystallography), the structure was not good enough to be certain that the hydrogen atoms occupy only the triangular face centers, because a phase transition of the crystal at the measurement temperature lowered the quality of the data set. There were negative peaks scattered throughout the unit cell with heights about the same as for the cluster hydrogen atoms.²¹ For this reason, another crystal, $[\text{PPh}_4]_3[\text{Zr}_6\text{Cl}_{18}\text{H}_5] \cdot 3\text{CH}_2\text{Cl}_2$, has now been measured. This structure shows clearly that the hydrogen atoms really reside only at the centers of the triangular faces. The results from this second neutron diffraction study are reported here.

The hydrogen atoms are found to be highly mobile at room temperature. In the cluster $[\text{Zr}_6\text{Cl}_{18}\text{H}_5]^{3-}$, the movement of the hydrogen atoms can be slowed down at low temperature, which results in extreme broadening of the resonance. It has also been found that one of the five hydrogen atoms in $[\text{Zr}_6\text{Cl}_{18}\text{H}_5]^{3-}$ can be removed by deprotonation with linear primary amines. The deprotonation reactions are sterically controlled by the available space on the Zr_3 triangular faces, as will be discussed here in terms of the structures of the hexazirconium clusters.

Experimental Section

Hexazirconium compounds are extremely air and moisture sensitive. All manipulations were conducted under an argon atmosphere by using standard vacuum line and Schlenk techniques. Glassware was oven dried at 150 °C for 24 h prior to use. Solvents were predried over molecular sieves and freshly distilled under nitrogen from appropriate drying reagents. NH_3 (0.5 M in 1,4-dioxane), MeNH_2 (2.0 M in THF), Me_2NH (2.0 M in THF), EtNH_2 (2.0 M in THF), Et_2NH (2.0 M in THF), Et_3N , (*n*-Bu) NH_2 , (*sec*-Bu) NH_2 , (*t*-Bu) NH_2 , Cy NH_2 (Cy = cyclohexyl), $\text{CH}_3(\text{CH}_2)_{17}\text{NH}_2$, pyridine (py), $\text{H}_2\text{PCH}_2\text{CH}_2\text{PH}_2$, and $[\text{PPh}_4]\text{Cl}$ were purchased from Aldrich. NH_3 and the amines in THF solutions as well as $\text{H}_2\text{PCH}_2\text{CH}_2\text{PH}_2$ were used as received. The other amines were distilled from P_2O_5 . Pyridine was distilled from CaH_2 . $[\text{PPh}_4]_3[\text{Zr}_6\text{Cl}_{18}\text{H}_5] \cdot 3\text{CH}_2\text{Cl}_2$,¹⁷ $[\text{PPh}_4]_4[\text{Zr}_6\text{Cl}_{18}\text{H}_4] \cdot 4\text{MeCN}$,¹⁸ and $[\text{PPr}_4]_3[\text{Zr}_6\text{Br}_{18}\text{H}_5]$ ¹⁵ were prepared by previously reported procedures. ^1H NMR spectra were collected either on a Varian-200E or a Unity Plus 300 spectrometer.

Reactions of $[\text{PPh}_4]_3[\text{Zr}_6\text{Cl}_{18}\text{H}_5]$. (1) With Linear Primary Amines. $[\text{PPh}_4]_3[\text{Zr}_6\text{Cl}_{18}\text{H}_5] \cdot 3\text{CH}_2\text{Cl}_2$ (**1**) (200 mg, 0.081 mmol) was dissolved in 15 mL of MeCN. To this purple solution was added dropwise 44 μmL (1.1 equiv) of 2.0 M EtNH_2/THF . The solution turned deep brown in 5 min. After 30 min of stirring, the solution was transferred to a Schlenk tube through a cannula and layered with 3 mL of hexanes and then 30 mL of Et_2O . Small block-shaped dark brown crystals of $[\text{EtNH}_3]_4[\text{Zr}_6\text{Cl}_{18}\text{H}_4] \cdot 4\text{MeCN}$ (**2**) (25 mg, 20%) on

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Table 1. Crystallographic Data for compounds [PPh₄]₃[Zr₆Cl₁₈H₅]·3CH₂Cl₂ (**1**), [PPh₄]₄[Zr₆Cl₁₈H₄]·4CH₂Cl₂ (**2**), and [H₃NEt]₄[Zr₆Cl₁₈H₄]·4MeCN (**3**)

compound	neutron	X-ray ^d	X-ray ^d	
		1	2	3
formula		C ₇₅ H ₇₁ Cl ₂₄ P ₃ Zr ₆	C ₁₆ H ₃₆ Cl ₁₈ N ₈ Zr ₆	C ₁₀₀ H ₉₂ Cl ₂₆ P ₄ Zr ₆
formula wt		2463.35	1525.04	2886.64
cryst syst		triclinic	tetragonal	tetragonal
space group		P1	P4 ₂ /mmm	I4 ₁ /a
<i>a</i> , Å	15.780(6)	15.993(3)	12.770(4)	26.441(5)
<i>b</i> , Å	21.96(3)	22.237(3)	12.770(4)	26.441(5)
<i>c</i> , Å	14.521(7)	14.670(4)	15.827(1)	16.0340(4)
α, (deg)	94.96(8)	95.31(1)	90	90
β, (deg)	111.59(4)	112.07(2)	90	90
γ, (deg)	81.72(5)	82.06(2)	90	90
<i>V</i> , Å ³	4627(11)	4784(2)	2581(1)	11210(3)
<i>Z</i>	2	2	4	4
<i>d</i> _{calcd} , g/cm ³	1.768	1.710	1.964	1.710
μ, cm ⁻¹	1.559	13.89	21.22	12.59
data collection instrument	SCD at BNL	CAD4	Nonius FAST	Nonius FAST
radiation (monochromated)	Ge (220) (λ = 1.15942 Å)	Mo Kα (λ = 0.70930 Å)	Mo Kα (λ = 0.70930 Å)	Mo Kα (λ = 0.70930 Å)
temp, K	15.0(1)	293(2)	213(2)	213(2)
2θ _{max} (deg)	74.5	45	50	45
no. of observs (<i>I</i> > 2σ(<i>I</i>))	3641 ^e	9573	1279	3647
no. of variables	737	1035	97	316
residuals (<i>R</i> ¹ , <i>wR</i> ²) ^b	0.132, 0.243	0.037, 0.096	0.039, 0.086	0.055, 0.101
goodness-of-fit indicators ^c	0.956	1.007	1.085	1.082
abs corrn	none	empirical	none	none

^a $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ (based on reflections with $F_o^2 > 2\sigma(F_o^2)$). ^b $wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.095P)^2]$; $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$ (also with $F_o^2 > 2\sigma(F_o^2)$). ^c Goodness-of-fit (on F^2) $S = [\sum [w(F_o^2 - F_c^2)^2] / (N_{\text{observs}} - N_{\text{params}})]^{1/2}$. ^d X-ray data from ref 17 for comparison. ^e No. of observs for $I > 2\sigma(I)$.

the wall of the Schlenk tube and large cubic dark brown crystals of [PPh₄]₄[Zr₆Cl₁₈H₄]·4MeCN (77 mg, 34%) on and close to the bottom of the tube were isolated after 10 days. Crystals of [PPh₄]₄[Zr₆Cl₁₈H₄]·4MeCN were identified by the unit cell parameters from the X-ray diffraction study.¹⁸ ¹H NMR for **2** (ppm, in CD₃CN): δ 7.40 (b, EtNH₃, 12H), 3.16 (m, CH₃CH₂NH₃, 8H), 1.21 (t, ³J_{H-H} = 7 Hz, CH₃CH₂NH₃, 12H), -5.19 (s, Zr₆H₄, 4H).

Reactions of **1** with other linear primary amines (MeNH₂, (*n*-Bu)NH₂, and CH₃(CH₂)₁₇NH₂) as well as NH₃ were carried out in a way similar to that described above. Formation of [Zr₆Cl₁₈H₄]⁴⁻ was detected by ¹H NMR spectroscopy. Because of the low solubility of compounds containing the cations [EtNH₃]⁺, [MeNH₃]⁺, and [NH₄]⁺ and difficulty in growing crystals for compounds containing cations with long linear hydrocarbon chains, in order to obtain accurate yields, the reactions were conducted in CH₂Cl₂ solution in the presence of an excess of [PPh₄]Cl (16.0 equiv). The product, [Zr₆Cl₁₈H₄]⁴⁻, was isolated as its [PPh₄]⁺ salt, [PPh₄]₄[Zr₆Cl₁₈H₄]·4CH₂Cl₂ (**3**). ¹H NMR for **3** (ppm in CD₃CN): δ 7.95 (m, P(C₆H₅)₄, 16H), 7.88 (m, P(C₆H₅)₄, 64H), -5.17 (s, Zr₆H₄, 4H). The yields for reactions with EtNH₂, MeNH₂, (*n*-Bu)NH₂, and CH₃(CH₂)₁₇NH₂ were 62, 57, 61, and 55%, respectively.

(2) With Other Lewis Bases. No reaction was observed between **1** and nonlinear primary amines (CyNH₂, (*sec*-Bu)NH₂, and (*t*-Bu)NH₂), secondary amines (Me₂NH and Et₂NH), tertiary amine (Et₃N), linear primary phosphine (H₂PCH₂CH₂PH₂), and py.

Reactions of [PPh₄]₄[Zr₆Cl₁₈H₄]. To the solution of [PPh₄]₄[Zr₆Cl₁₈H₄]·4MeCN (200 mg, 0.071 mmol) in 40 mL of MeCN was added slowly 155 μL (1.1 equiv) of 0.5 M NH₃/1,4-dioxane with vigorous stirring. A brown precipitate was formed instantly. The brown precipitate is not soluble in hexanes, C₆H₆, Et₂O, THF, MeCN, Me₂CO, py, and DMF. Attempts to solubilize it with (*n*-Bu)NH₂, Et₃N, PMe₂Ph, and [PPh₄]Cl in MeCN also failed.

No reaction was observed between [PPh₄]₄[Zr₆Cl₁₈H₄] and MeNH₂, Me₂NH, EtNH₂, Et₂NH, Et₃N, (*n*-Bu)NH₂, (*sec*-Bu)NH₂, (*t*-Bu)NH₂, CyNH₂, CH₃(CH₂)₁₇NH₂, py, and H₂PCH₂CH₂PH₂.

Reactions of [PPr₄]₃[Zr₆Br₁₈H₅]. No reaction was observed between [PPr₄]₃[Zr₆Br₁₈H₅] and NH₃, MeNH₂, Me₂NH, EtNH₂, Et₂NH, Et₃N, (*n*-Bu)NH₂, (*sec*-Bu)NH₂, (*t*-Bu)NH₂, CyNH₂, CH₃(CH₂)₁₇NH₂, py, and H₂PCH₂CH₂PH₂.

Crystallographic Studies. (1) X-Ray Diffraction. Crystals of **2** and **3** were mounted on the tip of a quartz fiber and placed in a cold stream of nitrogen at -60 °C. They were measured on an Enraf FAST

diffractometer with an area-detector and graphite-monochromated Mo Kα radiation. Preliminary data collection was carried out first to afford all cell parameters and an orientation matrix. Fifty reflections were used in indexing, and 250 reflections were used in cell refinement. Axial images were obtained to determine the Laue groups and confirm cell dimensions. Neither a decay nor an absorption correction was applied.²²

Structures were solved by a combination of direct methods using the SHELXS-86 program^{23a} and difference Fourier analyses using SHELXL-93.^{23b}

Compound **2** crystallized in the tetragonal crystal system. The space group *P*4₂/*m**m*m (No. 136) was assumed from the systematic absences in the data and confirmed by successful solution and refinement of the structure. The crystallographic data and results are listed in Table 1. The cluster anion, [Zr₆Cl₁₈H₄]⁴⁻, resides on a position of $\bar{4}$ symmetry. The cluster hydrogen atoms were located close to the centers of all the Zr₃ triangular faces of the Zr₆ cluster, but only one position (accounting for four of the eight positions in the cluster) was refined successfully with a fixed occupancy factor of 0.50, as inferred from a ¹H NMR study.¹⁸ The cation [EtNH₃]⁺ and solvate molecule MeCN were found to occupy the same 8-fold equipoint in such a way that there is one-half of each entity at each position. The structural data for [Zr₆Cl₁₈H₄]⁴⁻ are entirely consistent with those found in other [Zr₆Cl₁₈H₄]⁴⁻ compounds.¹⁸ This indicated that four counter ions, namely, [EtNH₃]⁺, are needed in compound **2**. For this reason, the occupancy factors for [EtNH₃]⁺ and MeCN were both assigned as 0.50, which resulted in there being four [EtNH₃]⁺ cations and four MeCN molecules per [Zr₆Cl₁₈H₄]⁴⁻ cluster. All non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms in the [EtNH₃]⁺ cation and the MeCN solvate molecule were calculated by assuming idealized geometry: C-H = 0.99 Å for the methyl group, 0.98 Å for the methylene group, and 0.94 Å for the phenyl group. They were included with fixed thermal parameters set at 1.5 *B*_{eq} and 1.2 *B*_{eq} of the corresponding carbon atom for the methyl group and the other groups, respectively.

(22) For more details concerning use of the area detector, see: Scheidt, W. R.; Turowska-Tyrk, I. *Inorg. Chem.* **1994**, *33*, 1314.

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Compound **3** crystallized in the tetragonal crystal system. The space group $I4_1/a$ (No. 88) was identified uniquely from the absences in the data. As in compound **2**, the cluster anion $[\text{Zr}_6\text{Cl}_{18}\text{H}_4]^{4-}$ again resides on a position of 4 symmetry. All non-hydrogen atoms were refined anisotropically. The cluster hydrogen atoms were located and refined successfully with fixed occupancy factors of 0.50 for each site, for the same reason mentioned before. The hydrogen atoms in the phenyl groups and CH_2Cl_2 solvate molecules were treated as described above for compound **2**.

(2) Neutron Diffraction. Crystals suitable for single-crystal neutron diffraction study were obtained from repeated recrystallization through slow diffusion of CH_2Cl_2 solutions of $[\text{PPh}_4]_3[\text{Zr}_6\text{Cl}_{18}\text{H}_5] \cdot 3\text{CH}_2\text{Cl}_2$ layered with THF. A block-shaped single crystal ($4.0 \times 3.2 \times 3.0$ mm) was chosen and mounted on an aluminum pin, using halocarbon grease (Dow-Corning), sealed in an aluminum container under a helium atmosphere, and placed in a DISPLEX Model CS-202 closed-cycle refrigerator (APD Cryogenics, Inc.). Following a preliminary examination at 240 K, the crystal was cooled to 15.0(1) K where the temperature was maintained throughout the measurements and monitored with a germanium resistance thermometer.

Neutron diffraction data were obtained on the four-circle diffractometer at beam port H6S of the High Flux Beam Reactor at Brookhaven National Laboratory. The neutron beam, monochromated by germanium (220) planes in transmission geometry, had a wavelength of 1.15942(10) Å as calibrated against KBr, $a_0 = 6.6000$ Å at 298 K. From $\sin^2 \theta$ values of 32 reflections ($35^\circ < 2\theta < 49^\circ$), the unit cell constants were determined to be $a = 15.780(6)$, $b = 21.96(3)$, and $c = 14.521(7)$ Å, $\alpha = 94.96(8)$, $\beta = 111.59(4)$, and $\gamma = 81.72(5)^\circ$, and $V = 4627(11)$ Å³.

Reflections were scanned for the hemisphere of reciprocal space, $+h, \pm k, \pm l$, for $5.8^\circ < 2\theta < 74.5^\circ$, using $\omega - 2\theta$ step scans. In the data collection, counts were accumulated at each step for a preset monitor count of the incident beam. Reflection scan widths in 2θ were as follows: 3.6° for $2\theta < 70^\circ$, and 4.0° for $70 < 2\theta < 74.5^\circ$, with steps of 0.06° in 2θ . Intensities of two reflections (2 0 -4 and 0 3 -3) were monitored every 200 reflections as a check on experimental stability, which proved to be excellent throughout. Altogether, 11 684 reflections were scanned. An azimuthal scan of two reflections (3 1 -1 and 9 1 0) near $\chi = 90^\circ$ showed no intensity variation.

Integrated intensities I_0 and variances $\sigma^2(I_0)$ were derived from the scan profiles as described previously.²⁴ Lorentz factors were applied. No absorption correction was applied, since the ψ -scans showed no variation, and neither was an extinction correction included. Averaging over 19 symmetry-related reflections gave an internal agreement factor on F^2 of 0.114. This resulted in 11 534 independent observations, 3519 of which had F_o^2 values greater than $3\sigma(F_o^2)$. The crystallographic data and results are also summarized in Table 1 with comparison to the corresponding X-ray data.

The atomic positions determined from the X-ray data¹⁷ were used to define a starting model. The structure model was refined based on 9569 independent F_o^2 values, using UPALS.^{25,26} The scale factor was varied, together with positional and isotropic displacement parameters for the 174 atoms comprising the asymmetric unit. The five hydrogen atoms of the $\text{Zr}_6\text{Cl}_{18}\text{H}_5$ unit were treated as being disordered over eight sites. A refinement including the site occupancy factors of these eight hydrogen positions resulted in a total of 5.3(1) hydrogen atoms, close to the expected number of 5. There are two independent halves of $[\text{Zr}_6\text{Cl}_{18}\text{H}_5]^{3-}$ cluster anions in the asymmetric unit. These are almost identical except for the distributions of hydrogen atoms on the Zr_3 faces. The distributions of hydrogen atoms on both are uneven. In one half unit, the occupancy factors are 0.48(8), 0.70(9), 0.77(9), and 0.72(10); in the other, they are 0.92(10), 0.82(10), 0.32(8), and 0.57(9). An anisotropic refinement resulted in numerous nonpositive definite atoms, probably due to the weak data, and it was decided to use the results of

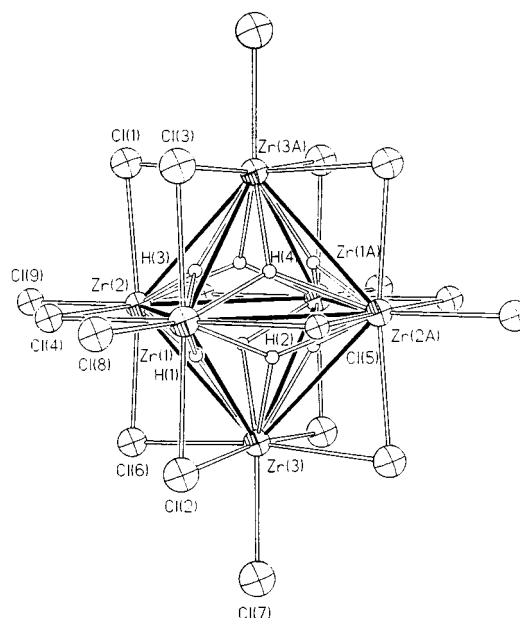


Figure 1. Neutron structure of one of the two independent $[\text{Zr}_6\text{Cl}_{18}\text{H}_5]^{3-}$ cluster anions in $[\text{PPh}_4]_3[\text{Zr}_6\text{Cl}_{18}\text{H}_5] \cdot 3\text{CH}_2\text{Cl}_2$ (**1**) showing 30% probability thermal ellipsoids. Hydrogen atoms are drawn with arbitrarily small ellipsoids for clarity.

the isotropic refinement. Using this model with 373 variables, after convergence was achieved with $\Delta p/\Sigma p < 0.1$, final agreement factors are as follows: $R(F_o^2) = 0.244$, $wR(F_o^2) = 0.132$, $S = 0.96$ with weights, $w^{-1} = \sigma^2$. The final difference-Fourier synthesis had no residual positive or negative peaks with scattering density exceeding 7% of that at the largest chlorine atom peak.

Results and Discussion

Although the cluster framework of $[\text{Zr}_6\text{Cl}_{18}\text{H}_5]^{3-}$ has been determined by X-ray crystallography and the number of hydrogen atoms well established by ^1H NMR spectroscopy,^{15,17} the hydrogen atoms in the cluster have not been unambiguously located. Neutron single-crystal diffraction provides a final solution to this problem. The neutron structure of $[\text{Zr}_6\text{Cl}_{18}\text{H}_5]^{3-}$ is shown in Figure 1. Selected bond lengths and angles, along with those from the X-ray diffraction study,¹⁷ are listed in Table 2. The cluster hydrogen atoms were located essentially at the centers of the eight triangular faces, as previously suggested by X-ray diffraction studies.^{15,17} The occupancy factor at each position ranges from 0.32 to 0.92 with an average of 0.66, which corresponds to a total of 5.3(1) hydrogen atoms per $[\text{Zr}_6\text{Cl}_{18}\text{H}_5]^{3-}$ cluster, in good accord with the correct value (5.0) obtained from a ^1H NMR study.^{15,17} The Zr-H distances vary from 1.90(4) to 2.02(6) Å with an average value of 1.96(4) Å, very close to that found with X-ray crystallography, 1.96(7) Å.¹⁵ The average distance between two adjacent hydrogen atoms is 1.49(6) Å, the shortest one of this kind ever observed in octahedral clusters. There are always three pairs of atoms on adjacent faces in a distribution of five atoms on eight faces of an octahedron.

With the hydrogen atoms residing on five of the eight Zr_3 triangular centers of the octahedron, some pairs of nonequivalent hydrogen atoms are linked by a bridging Zr atom. It should be possible to observe the coupling between these hydrogen atoms, as in compound $\text{Cp}_2\text{ZrH}\{\text{HAlR}_2\}_2\text{Cl}$ ($\text{R} = i\text{-butyl}$) (**D**) with $^2J_{\text{H-H}} = 7$ Hz.²⁷ However, the cluster hydrogen atoms were observed only as a slightly broad singlet signal at -3.07

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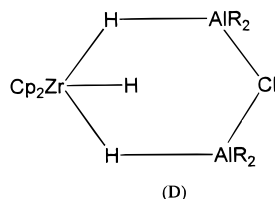
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Table 2. Selected Bond Lengths (Å) for the $[Zr_6Cl_{18}H_5]^{3-}$ Ion in **1**

	neutron	X-ray ¹⁷
Zr(1)–Zr(2)	3.40(1) ^a	3.403(1)
Zr(1)–Zr(3)	3.40(1)	3.406(1)
Zr(2)–Zr(3)	3.40(1)	3.397(1)
Zr(11)–Zr(12)	3.40(1)	3.3986(9)
Zr(11)–Zr(13)	3.43(1)	3.404(1)
Zr(12)–Zr(13)	3.39(1)	3.394(1)
Zr(2)–Cl(9)	2.47(1)	2.466(2)
Zr(1)–Cl(8)	2.52(1)	2.488(2)
Zr(3)–Cl(7)	2.481(9)	2.481(2)
Zr(11)–Cl(18)	2.52(1)	2.486(2)
Zr(12)–Cl(19)	2.49(1)	2.475(2)
Zr(13)–Cl(17)	2.517(9)	2.487(2)
Zr(1)–Cl(5)	2.55(1)	2.556(2)
Zr(1)–Cl(4)	2.57(1)	2.561(2)
Zr(1)–Cl(2)	2.577(9)	2.563(2)
Zr(1)–Cl(3)	2.587(9)	2.568(2)
Zr(2)–Cl(6)	2.561(9)	2.555(2)
Zr(2)–Cl(4)	2.59(1)	2.564(2)
Zr(2)–Cl(1)	2.590(9)	2.568(2)
Zr(2)–Cl(5)	2.59(1)	2.573(2)
Zr(3)–Cl(1)	2.591(9)	2.555(2)
Zr(3)–Cl(6)	2.56(1)	2.557(2)
Zr(3)–Cl(3)	2.59(1)	2.565(2)
Zr(3)–Cl(2)	2.59(1)	2.572(2)
Zr(11)–Cl(16)	2.56(1)	2.559(2)
Zr(11)–Cl(14)	2.58(1)	2.562(2)
Zr(11)–Cl(12)	2.596(9)	2.566(2)
Zr(11)–Cl(13)	2.548(9)	2.566(2)
Zr(12)–Cl(14)	2.57(1)	2.552(2)
Zr(12)–Cl(11)	2.561(9)	2.553(2)
Zr(12)–Cl(15)	2.569(9)	2.567(2)
Zr(12)–Cl(16)	2.57(1)	2.580(2)
Zr(13)–Cl(11)	2.54(1)	2.551(2)
Zr(13)–Cl(12)	2.60(1)	2.566(2)
Zr(13)–Cl(15)	2.57(1)	2.566(2)
Zr(13)–Cl(13)	2.549(9)	2.570(2)
Zr(1)–H(4)	1.99(3)	1.77(9)
Zr(1)–H(2)	1.92(3)	1.92(9)
Zr(1)–H(3)	1.93(3)	1.96(8)
Zr(1)–H(1)	1.99(3)	1.82(9)
Zr(2)–H(1)	1.95(4)	2.05(9)
Zr(2)–H(3)	1.96(3)	1.94(8)
Zr(3)–H(1)	1.95(4)	2.03(9)
Zr(3)–H(2)	2.00(3)	2.03(9)
Zr(11)–H(12)	1.91(4)	1.93(7)
Zr(11)–H(14)	1.94(5)	1.90(7)
Zr(11)–H(11)	1.95(3)	1.99(7)
Zr(11)–H(13)	2.02(6)	2.1(1)
Zr(12)–H(14)	2.01(4)	1.95(7)
Zr(12)–H(12)	1.98(4)	1.92(7)
Zr(13)–H(11)	1.93(3)	2.07(7)
Zr(13)–H(14)	2.01(4)	2.06(7)
Zr–Zr (average)	3.40(1)	3.396(3)
Zr–Cl _i (average)	2.50(1)	2.480(2)
Zr–Cl _h (average)	2.57(1)	2.563(2)
Zr–H (average)	1.96(4)	1.96(7)

^a Numbers in parentheses are estimated standard deviations in the least significant digits.



ppm.^{15,17} This is in contradiction to the fact that it is impossible to arrange five atoms in the same environment on the eight triangular face of an octahedron, implying that there should be more than one signal with splitting from the coupling between the different hydrogen atoms. One plausible explanation for

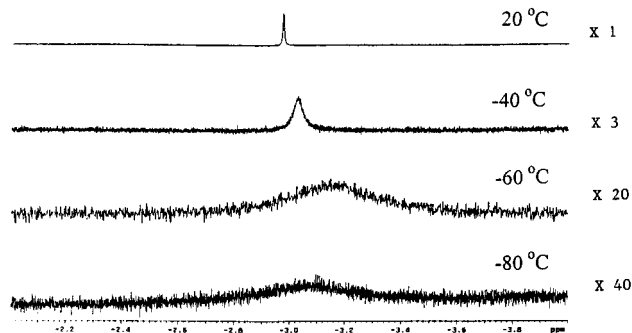


Figure 2. ¹H NMR spectra of $[PPh_4]_3[Zr_6Cl_{18}H_5] \cdot 3CH_2Cl_2$ (**1**) showing the signals of the cluster hydrogen atoms as a function of temperature.

the observed spectrum is that the hydrogen atoms are exchanging positions rapidly on the NMR time scale.

When the sample of $[PPh_4]_3[Zr_6Cl_{18}H_5]$ in acetone-*d*⁶ solution was cooled down, the signal of the cluster hydrogen atoms became broader and broader (Figure 2). It became a very broad peak at -80 °C and even broader at -90 °C, the lowest temperature attainable for solvents that dissolve the sample without obvious decomposition. The signal shifts upfield from 20 to -60 °C and then shifts downfield at lower temperature. Neither distinguishable signals from different hydrogen atoms nor the couplings between them were observed. It seems that at -60 °C the exchange of hydrogen atoms is still being observed.

There are probably two major factors contributing to the broadness of the signal at low temperature. One is an intermediate rate of exchange of hydrogen atoms. The lack of suitable solvents excludes the possibility of lowering the temperature to a point at which the hydrogen atoms are “frozen”, that is, exchanging extremely slowly. The other factor is the large number of couplings between the hydrogen atoms in different environments. The model of an octahedron in Figure 3a can be used to illustrate how many possible environments a hydrogen atom may have in the $[Zr_6Cl_{18}H_5]^{3-}$ cluster. By putting the hydrogen atom at the top triangular face, its environment is determined by the arrangements of the other four hydrogen atoms on the other seven triangular faces. If the edges connecting to the top face are cut apart, the other seven faces can be laid out as in Figure 3b with the central triangle corresponding to the face opposite to the top face in Figure 3a. There are 10 distinct possibilities for placing four atoms on the seven faces. This means that there is a total of 10 possible different environments for each hydrogen atom in $[Zr_6Cl_{18}H_5]^{3-}$. Since the hydrogen atoms exchange positions easily, we believe that the difference between any two of the possibilities is small. Therefore, at a particular moment these 10 possibilities are coexisting. In each possibility, the hydrogen atoms are not equivalent. For example, in the second possibility, there are three kinds of atoms. From coupling with these three kinds of hydrogen atoms, the hydrogen atom on the top face will be observed as a doublet doublet triplet, with totally $2 \times 2 \times 3 = 12$ components to the signal. Because of the small difference among the ten possibilities, it is likely that the signals of these possibilities will be overlapping to form a very broad peak even when the hydrogen atoms are “frozen”. Coupling between ⁹¹Zr (natural abundance of 11.23%) with $I = 5/2$ and the hydrogen atoms may also contribute to the broadness of the signal.

There are only a few other hexanuclear octahedral clusters in which the hydrogen atom(s) have been well characterized by neutron diffraction. A distribution of hydrogen atoms similar to that in $[Zr_6Cl_{18}H_5]^{3-}$ was observed in $[Th_6Br_{15}D_7]$ where the

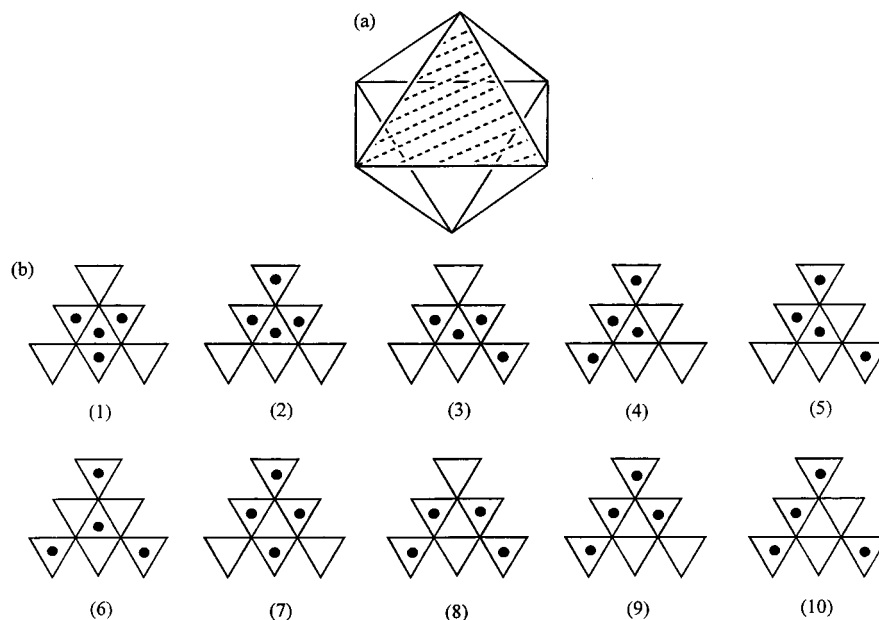
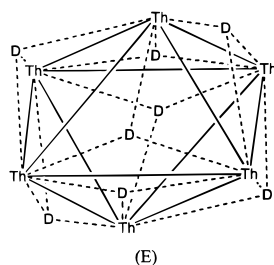


Figure 3. (a) Octahedron representing the Zr_6 cluster. (b) Ten possibilities to arrange four atoms on seven triangular faces of the Zr_6 octahedron.

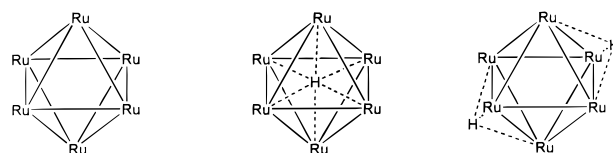
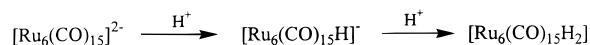
seven deuterium atoms were found to be disordered over the eight Th_3 faces of the octahedral cluster (*E*).^{8b} In this case the



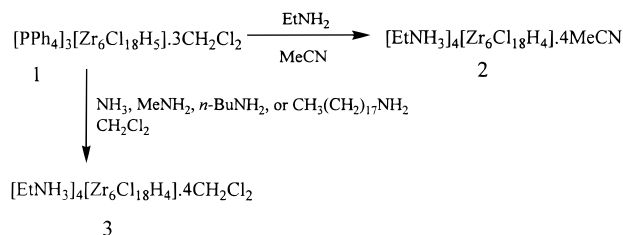
hydrogen atoms are actually sitting above the triangular faces, and the Th–Th distances (average 3.861(2) Å) are so much larger than the Zr–Zr distances (average 3.400(1) Å in $[Zr_6Cl_{18}H_5]^{3-}$)¹⁷ so that the shortest distance between two hydrogen atoms is 2.050(3) Å, much longer than that in $[Zr_6Cl_{18}H_5]^{3-}$, 1.49(6) Å. In another class of hexanuclear octahedral clusters containing more than one hydrogen atom, $[Cu_6(PR_3)_6H_6]$,^{8a} a neutron diffraction study of $[Cu_6\{P(p\text{-tolyl})_3\}_6H_6]$ showed that the six hydrogen atoms reside above six of the eight Cu_3 faces, similar to $[Th_6Br_{15}D_5]$ but without disorder. The hydrogen atoms are almost as well separated, with the shortest distance between two adjacent hydrogen atoms being 1.97(6) Å. There are some hexanuclear clusters containing only one hydrogen atom which were also studied by neutron diffraction, namely, $[Nb_6I_{11}H]$,^{7a} $[Co_6(CO)_{15}H]^-$,^{7b} and $[Ru_6(CO)_{15}H]^-$.^{7c} In these three clusters, the hydrogen atom was found at the center of the cluster.

The distance between the two closest hydrogen atoms in $[Zr_6Cl_{18}H_5]^{3-}$ (1.49(6) Å) is too long for any bonding between them. At this distance, there is no evidence indicating if there is repulsion or attraction between them. It seems that there is repulsion when the hydrogen atoms are too close since the hydrogen atoms in $[Cu_6\{P(p\text{-tolyl})_3\}_6H_6]$ ^{7a} and $[Th_6Br_{15}D_7]$ ^{7b} lie a little outside the cluster octahedron. There is a tendency regarding the arrangement of hydrogen atoms in the octahedral clusters. When there is only one hydrogen atom, the hydrogen atom is located at the center of the octahedron, such as in $[Nb_6I_{11}H]$,^{7a} $[Co_6(CO)_{15}H]^-$,^{7b} and $[Ru_6(CO)_{15}H]^-$.⁷ When there are more hydrogen atoms in the cluster, they tend to arrange above the triangular faces outside the octahedron, as in

Scheme 1



Scheme 2



$[Zr_6Cl_{18}H_5]^{3-}$, $[Cu_6\{P(p\text{-tolyl})_3\}_6H_6]$,^{8a} and $[Th_6Br_{15}D_7]$,^{8b} depending on the length of the metal–hydrogen bond. This can be further illustrated in the following protonation reactions of the $[Ru_6(CO)_{15}]^{2-}$ clusters (Scheme 1).²⁷ When the empty cluster $[Ru_6(CO)_{15}]^{2-}$ is treated with acid, a proton goes to the center of the cluster to be a μ_6 interstitial hydrogen atom. A similar reaction was observed in the protonation of $[Co_6(CO)_{15}]^{2-}$ to form $[Co_6(CO)_{15}H]^-$.^{7b} Upon addition of another proton to the $[Ru_6(CO)_{15}H]^-$ cluster, both hydrogen atoms then lie above two opposite faces as determined from X-ray diffraction; the atom originally at the center was obviously moved outside.

The hydrogen atom in $[Co_6(CO)_{15}H]^-$ can be removed with weak Lewis bases, for example, H_2O , $MeOH$, *i*- $PrOH$, and THF .^{7b} Deprotonation reactions were also observed in our hexazirconium clusters, $[Zr_6Cl_{18}H_5]^{3-}$ and $[Zr_6Cl_{18}H_4]^{4-}$. When the $[Zr_6Cl_{18}H_5]^{3-}$ cluster was treated with 1 equiv of ammonia or linear primary amines, RNH_2 ($R = Me, Et, n\text{-Bu}$, and $CH_3(CH_2)_{17}$), one of the five hydrogen atoms was removed by one amine molecule to form an ammonium cation, RNH_3^+ , which was characterized by 1H NMR spectroscopy. The cluster was converted into $[Zr_6Cl_{18}H_4]^{4-}$ (Scheme 2), which has been previously prepared by substitution of phosphine ligands in $[Zr_6$

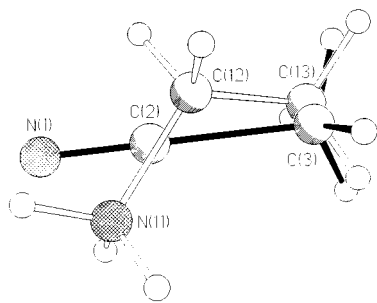


Figure 4. Illustration showing the disorder of the $[EtNH_3]^+$ cation and MeCN solvate molecule in $[EtNH_3]_4[Zr_6Cl_{18}H_4] \cdot 4MeCN$ (**2**). Carbon atoms and nitrogen atoms are represented with 30% probability thermal ellipsoids. Hydrogen atoms are drawn with arbitrarily small ellipsoids for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[EtNH_3]_4[Zr_6Cl_{18}H_4] \cdot 4MeCN$ (**2**)

Zr(1)–Zr(2)	3.360(1) ^a	Zr(1)–Cl(2)	2.571(1)
Zr(1)–Zr(1A)	3.355(1)	Zr(2)–Cl(3)	2.566(1)
Zr(1)–Zr(1B)	3.378(1)	N(1)–C(2)	1.08(2)
Zr(1)–Cl(4)	2.555(1)	C(2)–C(3)	1.62(4)
Zr(2)–Cl(5)	2.560(2)	N(11)–C(12)	1.46(1)
Zr(1)–Cl(3)	2.565(1)	C(12)–C(13)	1.27(4)
Zr(1)–Cl(1)	2.567(2)		
Zr(1A)–Zr(1)–Zr(2)	60.05(1) ^a	Zr(1B)–Zr(2)–Zr(1A)	90.23(2)
Zr(2)–Zr(1)–Zr(1B)	59.821(9)	Zr(1A)–Cl(1)–Zr(1)	81.61(6)
Zr(1B)–Zr(2)–Zr(1)	60.36(2)	Zr(1)–Cl(2)–Zr(1B)	82.14(6)
Zr(1)–Zr(2)–Zr(1A)	59.91(2)	Zr(1A)–Cl(3)–Zr(2)	81.79(3)
Zr(2)–Zr(1)–Zr(2A)	89.77(2)	N(1)–C(2)–C(3)	180(2)
Zr(1A)–Zr(1)–Zr(1B)	90.0	C(13)–C(12)–N(11)	117(2)
Zr(1A)–Zr(2)–Zr(1)	90.23(2)		

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

$Cl_{14}(PR_3)_4H_4$ with Cl^- .¹⁸ In the reaction of $[PPh_4]_3[Zr_6Cl_{18}H_5]$ with $EtNH_2$ in MeCN, the products ($[Zr_6Cl_{18}H_4]^{4-}$ and $[EtNH_3]^+$) cocrystallized as $[EtNH_3]_4[Zr_6Cl_{18}H_4] \cdot 4MeCN$ (**2**) and the cation, $[EtNH_3]^+$, was characterized crystallographically, as shown in Figure 4. An interesting and novel disorder was observed, where $[EtNH_3]^+$ and MeCN each partially occupy the same crystallographic site. The important bond distances and angles of $[Zr_6Cl_{18}H_4]^{4-}$ in **2** are given in Table 3. The structural data for the framework of the $[Zr_6Cl_{18}H_4]^{4-}$ in **2** are almost identical to those reported before with different cations.¹⁸ When the deprotonation reactions with NH_3 , $MeNH_2$, and $CH_3(CH_2)_{17}NH_2$ were carried out in CH_2Cl_2 solution in the presence of excess of $[PPh_4]Cl$, the cluster product was isolated as $[Zr_6Cl_{18}H_4] \cdot 4CH_2Cl_2$ (**3**). Compound **3** was characterized by 1H NMR and X-ray diffraction. The four hydrogen atoms in $[Zr_6Cl_{18}H_4]^{4-}$ were found to be distributed essentially at the centers of the eight Zr_3 faces in a similar way to that in $[Zr_6Cl_{18}H_5]^{3-}$. The structure of $[Zr_6Cl_{18}H_4]^{4-}$ from **3** is shown in Figure 5. Selected bond lengths and angles are given in Table 4. The average distance $Zr-H = 1.94$ Å.

Primary amines with branched hydrocarbon chains ($CyNH_2$, $sec-BuNH_2$, and $t-BuNH_2$), secondary amines (Me_2NH and Et_2NH), py , and a tertiary amine (Et_3N) did not react with $[Zr_6Cl_{18}H_5]^{3-}$ at all. Obviously, this reaction is sterically controlled by the shape of the molecule of Lewis base. We know of no other example of such a sterically controlled reaction for a hydrogen-containing cluster.

This steric control is the result of the arrangement of the three bridging Cl atoms over the Zr_3 face (Figure 1). It was reported that the hydrogen atom in $[Co_6(CO)_{15}H]^-$ appeared to be able to "walk" out of the octahedral cluster cage to react with Lewis bases.^{7b} However, in the deprotonation of $[Zr_6Cl_{18}H_5]^{3-}$, it

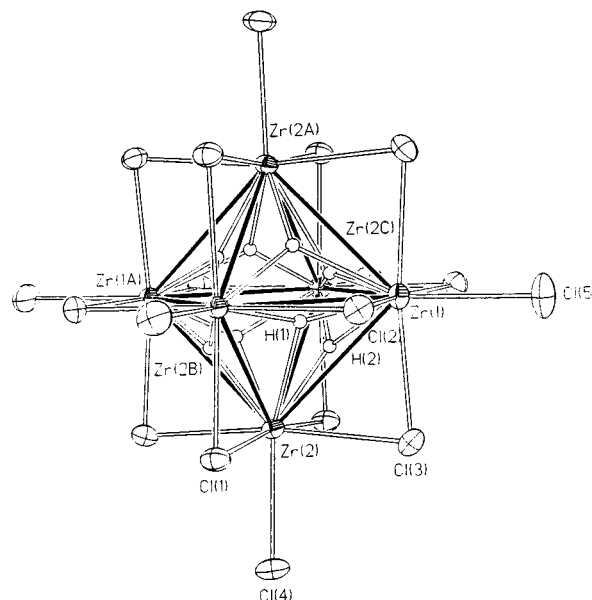


Figure 5. X-ray structure of $[Zr_6Cl_{18}H_4]^{4-}$ in $[PPh_4]_4[Zr_6Cl_{18}H_4] \cdot 4CH_2Cl_2$ (**3**) showing 30% probability thermal ellipsoids. Hydrogen atoms are drawn with arbitrarily small ellipsoids for clarity.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $[PPh_4]_4[Zr_6Cl_{18}H_4] \cdot 4CH_2Cl_2$ (**3**)

Zr(1)–Zr(2)	3.376(1)	Zr(2)–Cl(3)	2.564(2)
Zr(1)–Zr(2B)	3.3580(9)	Zr(2)–Cl(1C)	2.565(2)
Zr(1)–Zr(2C)	3.3580(9)	Zr(2)–Cl(1)	2.574(2)
Zr(2)–Zr(1B)	3.3579(9)	Zr(2)–Cl(2C)	2.577(2)
Zr(2)–Zr(2B)	3.363(1)	Zr(1)–H(1)	1.6(3)
Zr(2)–Zr(2C)	3.363(1)	Zr(1)–H(1A)	1.6(3)
Zr(2)–Cl(4)	2.551(2)	Zr(1)–H(2A)	2.1(2)
Zr(1)–Cl(5)	2.539(3)	Zr(1)–H(2)	2.1(2)
Zr(1)–Cl(2A)	2.568(2)	Zr(2)–H(2)	1.8(2)
Zr(1)–Cl(3)	2.576(2)	Zr(2)–H(1C)	1.9(3)
Zr(1)–Cl(3A)	2.576(2)	Zr(2)–H(2B)	2.0(2)
Zr(1)–Cl(2)	2.568(2)	Zr(2)–H(1)	2.4(4)
Zr(2B)–Zr(1)–Zr(2)	59.92(2)	Zr(2)–Cl(3)–Zr(1)	82.12(6)
Zr(2C)–Zr(1)–Zr(2)	59.92(2)	Zr(1)–H(1)–Zr(2B)	139(10)
Zr(1B)–Zr(2)–Zr(2B)	60.31(2)	Zr(1)–H(1)–Zr(2)	113(10)
Zr(1B)–Zr(2)–Zr(2C)	60.31(2)	Zr(2B)–H(1)–Zr(2)	102(10)
Zr(2B)–Zr(1)–Zr(2C)	90.18(3)	Zr(2)–H(2)–Zr(2C)	126(10)
Zr(2B)–Zr(2)–Zr(2C)	90.0	Zr(2)–H(2)–Zr(1)	122(10)
Zr(2B)–Cl(1)–Zr(2)	81.77(5)	Zr(2C)–H(2)–Zr(1)	112(9)
Zr(1)–Cl(2)–Zr(2B)	81.49(6)		

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

seems that the base molecule has to go through the limited space shaped by the three bridging Cl atoms (Figure 6). The atoms in Figure 6 are represented by balls with covalent radii of the corresponding elements. In reality, the Cl atoms might be larger and the Zr atoms smaller. In $[Zr_6Cl_{18}H_5]^{3-}$, the distance from the boundary of Cl balls to the center of the triangle formed by the three Cl atoms is $a = 0.97$ Å, and the distance between the boundaries of two Cl balls is $b = 1.65$ Å. Adoption of an approach with the incoming amine molecule staggered with the three Cl atoms certainly will reduce the repulsion between the cluster and the base molecule. Even though the space among three Cl atoms is enough to accommodate the N atom ($r = 0.75$ Å), the space between two Cl atoms is not large enough for the $-CH_2-$ group. In order to go through the barrier, the alkyl group in the amine molecule has to tilt toward the center. The depth of the hole is 2.91 Å. This prohibits that there be any substituent group at the α -C atom. The primary amine molecules with alkyl groups branched at the α -C atom (such as $CyNH_2$, $CH_3CH_2CH(CH_3)NH_2$, and $(CH_3)_3CNH_2$, and py)

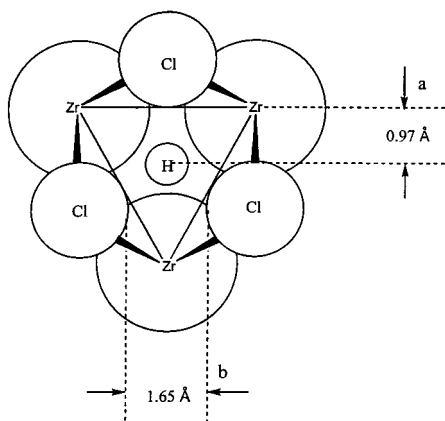


Figure 6. Ball model showing one of the eight triangular faces with three bridging chlorine atoms of the Zr₆ cluster: (a) is the distance between the boundary of a Cl ball to the center of the triangle formed by the three Cl atoms; (b) is the distance from the boundaries of two Cl balls.

are too large for the limited space and cannot gain access to the cluster hydrogen atoms at the centers of the Zr₃ faces. Secondary and tertiary amine molecules are even bigger so that there is no reaction between them and [Zr₆Cl₁₈H₅]³⁻. The determining factor in the deprotonation reactions is the shape of the amine molecule in the region of the N atom, not the length of it. This was proved by using the linear octadecyl amine (CH₃(CH₂)₁₇NH₂) to remove one of the hydrogen atoms from the cluster.

Although linear primary amines react readily with the [Zr₆Cl₁₈H₅]³⁻ cluster, there is no reaction between the cluster and primary phosphine H₂PCH₂CH₂PH₂. Apparently the space limitation might play an important role here since the phosphorus atom with a covalent radius of 1.06 Å is too large for the available space (*a* = 0.97 Å). The lower basicity of the phosphine compared to the primary amines may also play a role. Basicity in itself is also important here. For example, MeCN, a very weak base, cannot remove a hydrogen atom from [Zr₆Cl₁₈H₅]³⁻, even though this molecule is small enough to penetrate to the hydrogen atom. The [Zr₆Cl₁₈H₅]³⁻ is stable in MeCN solution.

While the use of linear primary amines provides an excellent means of removing a hydrogen atom from [Zr₆Cl₁₈H₅]³⁻ to form [Zr₆Cl₁₈H₄]⁴⁻, no further removal of hydrogen atoms can be accomplished by this method. There is no reaction between [Zr₆Cl₁₈H₄]⁴⁻ and linear primary amines. In fact, no matter how much amine is used, the reaction of [Zr₆Cl₁₈H₅]³⁻ with linear primary amines always stops at the [Zr₆Cl₁₈H₄]⁴⁻ product. The framework of the [Zr₆Cl₁₈H₄]⁴⁻ cluster¹⁸ is almost identical to that of [Zr₆Cl₁₈H₅]³⁻ species, but with slightly smaller dimensions (Zr–Zr = 3.400(1) Å in [Zr₆Cl₁₈H₅]³⁻ vs 3.366(1) Å in [Zr₆Cl₁₈H₄]⁴⁻). This results in a smaller space available on the triangular faces with *a* = 0.95 Å and *b* = 1.39 Å. The dramatic shrinkage of *b*, which is important to accommodate the alkyl group, makes it impossible for the amine molecules to access to the hydrogen atoms. When ammonia, an amine without an alkyl group, was used, the ammonia molecule did react with [Zr₆Cl₁₈H₄]⁴⁻. Unfortunately, this reaction resulted in the formation of an insoluble product which cannot be characterized by available methods. Another factor, of course, is the greater resistance of a species with a –4 charge to proton loss.

Because of the large size of the Br atom, the hole in the [Zr₆Br₁₈H₅]³⁻ cluster is even smaller,^{15,28} *a* = 0.84 Å and *b* =

1.16 Å, than those in the Cl species. The distance between the boundary of a Br ball and the center of the triangle of the three Br atoms is 0.84 Å, only slightly larger than the covalent radius of a N atom, *r* = 0.75 Å. The available space in [Zr₆Br₁₈H₅]³⁻ is too small even for the ammonia molecule. No reaction of [Zr₆Br₁₈H₅]³⁻ with linear primary amines or ammonia was observed.

Even though one of the five hydrogen atoms in [Zr₆Cl₁₈H₅]³⁻ can easily be extracted with linear primary amines to form [Zr₆Cl₁₈H₄]⁴⁻, attempts to protonate [Zr₆Cl₁₈H₄]⁴⁻ to form [Zr₆Cl₁₈H₅]³⁻ have failed. Treatment of [Zr₆Cl₁₈H₄]⁴⁻ with HCl/CH₂Cl₂ and HBF₄/Et₂O led to the rupture of the cluster to form [ZrCl₆]²⁻ and H₂.¹⁹ In this process, it is possible that the proton was attached to the Cl atom with negative charge and caused the decomposition of the cluster instead of being delivered to the Zr₆ cluster. This behavior is different from that of the carbonyl clusters [M₆(CO)₁₅]²⁻ (M = Co,^{7b} Ru^{7c}) which can easily be protonated with acid.

The distance between two Zr atoms in [Zr₆Cl₁₈H₅]³⁻ is significantly greater than the Zr–Zr single bonds in the octahedral face-sharing compounds [Cl₂(PR₃)₂Zr(μ-Cl)₂ZrCl₂(PR₃)₂], mean value of 3.396(3) Å (X-ray) vs 3.132(1) Å in [Zr₂Cl₆(PMe₃)₄].²⁹ Surprisingly, it is impossible to break the Zr–Zr bond in the cluster with strong ligands such as amines, phosphines, and Cl⁻. Cl⁻ have been shown to be able to coordinate to Zr atoms more strongly than phosphines.¹⁸ The cluster is also inert toward phenylacetylene and H₂. No H/D exchange between [Zr₆Cl₁₈D₅]³⁻ and H₂ was observed at room temperature in CH₂Cl₂ solution.

Concluding Remarks

A 14-electron closed-shell configuration is important for hexazirconium clusters. The clusters may use an interstitial atom (Z) to achieve this stable configuration.³ They can also incorporate more than one hydrogen atom as shown for the hexazirconium clusters. In contrast to the clusters containing only one hydrogen atom which resides at the center,⁷ the hydrogen atoms in [Zr₆Cl₁₈H₅]³⁻ are distributed on the Zr₃ triangular faces. The results from the neutron diffraction study also confirmed our findings from X-ray diffraction studies and a previous neutron study that the hydrogen atoms in our hexazirconium clusters containing two or more hydrogen atoms are distributed in a similar way.

These clusters are the first hexanuclear cluster systems containing more than one hydrogen atom that have ever been studied in solution. Because of the steric barrier from the bridging Cl atoms, the [Zr₆Cl₁₈H₅]³⁻ cluster shows size-selective reactivity toward amine bases. Only amines small enough to penetrate the barrier can deprotonate the cluster by one hydrogen atom.

The hydrogen atoms in all hexazirconium clusters move around rapidly at room temperature. The rapid exchange explains why the hydrogen atoms are always observed as a singlet in NMR studies without coupling to one other or to deuterium atoms in the case of [Zr₆Cl₁₈(H_{1/2}D_{1/2})₅]³⁻¹⁷ and phosphorus atoms in [Zr₆Cl₁₄H₄(PR₃)₄].¹⁶ Neither ¹H–¹³C coupling in [Ru₆(CO)₁₅H]^{-7c} nor D–P coupling in [Cu₆{P(NMe₂)₃}₆H₆]³⁰ was detected, probably for the same reason. The observations of the arrangement of hydrogen atoms from X-ray diffraction studies at room temperature are the statistical result of the exchange of positions on the eight triangular faces. This distribution is usually even,^{11–21} as was the distribution

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of the seven deuterium atoms on eight Th₃ faces in [Th₆-Br₁₅D₇].^{8b} However, at very low temperature, as in this neutron diffraction study, the hydrogen atoms are presumably "frozen" at random positions, giving rise to the observation that they appear to be disordered on eight faces.

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Supporting Information Available: Tables of data collection and refinement details, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters (18 pages). See any current masthead page for ordering and Internet access instructions.

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