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Stabilization by Hydrogen. Synthetic and Structural Studies of the Zintl Phase $Ba_5Ga_6H_2$

Robert W. Henning, E. Alejandro Leon-Escamilla, Jing-Tai Zhao, and John D. Corbett*

Department of Chemistry and Ames Laboratory—DOE,[1] Iowa State University, Ames, Iowa 50011

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Synthesis of the phase formerly reported as Ba_5Ga_6 succeeds only in the presence of hydrogen. The heavy atom structure of $Ba_5Ga_6H_2$ has been redetermined by single-crystal X-ray diffraction (trigonal $P\bar{3}c1$, $Z = 2$, $a = 7.7698(2)$ Å, $c = 14.3902(7)$ Å), and the hydrogen positions have been elucidated by time-of-flight neutron powder diffraction. The unit cell contains isolated slightly distorted octahedra Ga_6^{8-} with barium cations over all edges. Hydride is bound in two types of barium tetrahedra [$d(Ba-H) = 2.61-2.62$ Å]. The stoichiometry is appropriate for a Zintl phase: $(Ba^{2+})_5Ga_6^{8-}(H^-)_2$.

Introduction

The compound Ba_5Ga_6 and its structure were originally reported by Fornasini and Pani[2] in 1994. The composition and structure were determined by single-crystal X-ray diffraction. An interesting observation was the apparent excess of two electrons per anion when Wade−Mingos[3] rules were applied. Compounds composed of alkaline-earth and main-group elements are frequently Zintl phases which conform to octet valence rules.[4] A classical isolated gallium octahedron would be formulated as Ga_6^{8-}, but according to the number of cations, the cluster in this binary compound would either appear to have a charge of 10− or the phase should be metallic. Alternatively, the apparent excess of two electrons might mean that an interstitial impurity with a cumulative charge of 2− per formula unit was present. Adventitious hydrogen, as well as other light elements that are difficult to detect by X-rays, have frequently been found to yield new compounds. Hydrogen stabilization has been found by Leon-Escamilla and Corbett[5] to be present in all examples of the supposed Yb_5Sb_3 structure type[5] as well as in many other compounds.[6] In the Ba_5Ga_6 case, two hydride anions per formula unit would satisfy the Zintl−Klemm valence rules,[4] viz. $(Ba^+)_5Ga_6^{8-}(H^-)_2$. Most commercial barium contains significant amounts of hydrogen (10−20 at. % or more),[7] and unexpected hydrides can form if precautions are not taken to remove the hydrogen.

A theoretical investigation of this compound and the Ga_6 cluster has been reported by Liu et al.,[8] considering the probable effect of two extra electrons on the cluster. Extended Hückel calculations indicated that a cluster formulated as Ga_6^{10-} or with appreciable electron density in the LUMO orbitals of Ga_6^{8-} from metal-like electrons should exhibit a Jahn−Teller distortion which should reduce the symmetry to D_{4h} or D_{3d}. The observed cluster is relatively undistorted in comparison with full octahedral symmetry. Their calculations thus indirectly supported the concept that hydrogen is stabilizing the compound.

In this paper, we report the synthetic evidence that hydrogen is required for the formation of "Ba_5Ga_6" as well as an improved single-crystal X-ray refinement and verification of the ternary structure of $Ba_5Ga_6H_2$ by neutron diffraction by a deuterated sample.

Experimental Section

Syntheses. All materials were handled in a He-filled glovebox to reduce contamination. Sublimed barium (AAPL, Urbana, IL) sealed in a tantalum container was heated at about 700 °C under dynamic vacuum ($\leq 10^{-5}$ Torr) for 12 h to remove hydrogen. Barium hydride (deuteride) was prepared by heating barium metal for an additional 12 h under 1 atm of excess H_2 (D_2) at the same temperature. Guinier powder patterns of the white powder indicated that only BaH_2 (BaD_2) was present. Barium, gallium (99.99%, Johnson-Matthey), and barium hydride were initially sealed in tantalum tubing to give a final stoichiometry of $Ba_5Ga_6H_2$. The container was in turn sealed in an evacuated silica container to avoid air attack at high temperatures.[9] This first run explored a wide range of conditions. It was heated to 600 °C, held at that temperature for 24 h, and then heated to 1050 °C over 5 h and annealed for 1.5 h. The sample was next allowed to cool radiatively to 750 °C, held for $^1/_2$ h, cooled at a rate of 5° h^{-1} to 560 °C followed by 15 h of annealing, cooled (30° h^{-1}) to 350 °C, and finally annealed for 8 h. The final product contained 15% $Ba_5Ga_6H_2$. Higher yields (up to ~70%) of $Ba_5Ga_6H_2$ could be obtained with excess hydrogen ($Ba_5Ga_6H_4$) and slow cooling from 1100 °C at a rate of 5° h^{-1}. After the diffraction experiments were finished, a virtually quantitative synthesis (~95%) was achieved by reaction of a $Ba_6Ga_6H_{0.67}$ composition for 4 h at 1100 °C followed by cooling at 20° h^{-1} to room temperature. Conversely, the same reactions carried out with the Ta container held in high vacuum never produced the target phase since hydrogen (deuterium) diffuses through Ta at temperatures above ~550 °C.

Deuteride samples were loaded in the same manner as the hydride synthesis but with BaD_2 instead of BaH_2 and with an overall stoichiometry of $Ba_5Ga_6D_4$. Six separate reactions were loaded, each with 1.0 g of material, since previous experiments had indicated that smaller sized samples produced higher yields of the desired phase. Each tantalum tube was sealed in a separate silica jacket in order to maintain a low deuterium pressure. The samples were placed into a furnace preheated to 800 °C, rapidly heated to 1100 °C, and held there for 3 h. The samples were cooled at a rate of 5° h^{-1} to 300 °C then at 10° h^{-1} to room temperature. The main product in each reaction was $Ba_5Ga_6D_2$ (65−70%), but $BaGa_2$ (AlB_2 type) (25−30%) and BaD_2 (1−5%) were also observed. Two of the six samples contained some weak unidentified lines in the powder patterns so those reactions were not included in the final sample. The identified side products could not be separated so 3.78 g of the mixture was sealed into a vanadium cylinder under helium for the neutron diffraction experiment.

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(2) Fornasini, M. L.; Pani, M. *J. Alloys Comp.* **1994**, *205,* 179.

(3) Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley-Interscience: New York, 1985; Chapter 22.

(4) *Chemistry, Structure and Bonding in Zintl Phases and Ions*; Kauzlarich, S., Ed.; VCH: New York, 1996.

(5) Leon-Escamilla, E. A.; Corbett, J. D. *J. Alloys Comp.* **1994**, *206*, L15.

(6) Leon-Escamilla, E. A. Ph.D. Dissertation, Iowa State University, 1996.

(7) Peterson, D. T. *J. Met.* **1987**, *39*, 20; private communication, 1992.

(8) Liu, Q.; Hoffmann, R.; Corbett, J. D. *J. Phys. Chem.* **1994**, *98*, 9360.

(9) Sevov, S. C.; Corbett, J. D. *Inorg. Chem.*, **1992**, *31*, 1895.

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Table 1. Single-Crystal X-ray Data Collection and Refinement Parameters for $Ba_5Ga_6H_2$

fw	1106.98
space group, Z	$P3c1$ (No. 158), 2
lattice params[a]	
a, Å	7.7698(2)
c, Å	14.3902(7)
V, Å^3	752.35(1)
d_{calc}, g/cm^3	4.916
temp, °C	23
μ, cm^{-1} (Mo Kα)	234.89
residuals: R, R_w,[b] %	4.3, 4.7

[a] Guinier data with Si as an internal standard; $\lambda = 1.540\,562$ Å, 23 °C. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$, $w = 1/\sigma^2$.

Table 2. Powder Neutron Data Collection and Refinement Parameters

temp, °C	23
no. of data	10 747
params[a]	61
residuals; R_p, R_{wp},[b] %	1.88, 2.94
χ^2	11.85
scattering lengths ($\times 10^{-12}$ cm)[c]	
Ba	0.525
Ga	0.729
D	0.6674

[a] Includes proportions of $BaGa_2$ and BaH_2 impurities. [b] $R_p = (\sum|I_o - I_c|)/\sum I_o$; $R_{wp} = [\sum(I_o - I_c)^2/\sum wI_o^2]^{1/2}$. [c] Reference 14.

Structural Studies. Selected crystals of the protide were sealed in thin-walled capillaries and checked for singularity by Laue photographs. X-ray data were collected on a CAD4 single-crystal diffractometer at room temperature with the aid of Mo Kα radiation. Twenty-five reflections located by a random search were used to determine the hexagonal unit cell. Four octants of data ($h,\pm k,\pm l$) were collected at room temperature and corrected for Lorentz and polarization effects. A total of 6629 reflections were measured up to $2\theta = 60°$, of which 2498 were unique and observed ($I \geq 3\sigma_I$). The data were also corrected for absorption with the aid of the average of three ψ-scans ($\mu = 233$ cm^{-1}).

Systematic absences and Wilson plot statistics did not indicate a unique space group. Fornasini and Pani refined the structure in space group $P\bar{6}c2$ (No. 188),[2] but this resulted in a split barium position. Closer inspection of the structure suggested that the split position could have been caused by twinning about the x, y, $^1/_4$ mirror plane. If this mirror plane is removed, along with any symmetry-related ones, the remaining operations define space group $P3c1$ (No. 158). Refinement of our data in this asymmetric space group proceeded without complications. Direct methods[10] revealed three barium and two gallium positions. The atomic positions and thermal parameters were refined with the TEXSAN[11] package on a VAX station. After the isotropic refinement the data were further corrected for absorption by DIFABS,[12] averaged, and refined to give a final $R(F)/R_w$ factors of 4.3/4.7% at convergence. Some selected crystallographic data are listed in Table 1. Additional data collection and refinement parameters and anisotropic thermal parameters are given in the Supporting Information. These and the F_o/F_c listing are also available from J.D.C.

The neutron data were collected at 23 °C on the high-intensity powder diffractometer (HIPD) at the Los Alamos Neutron Scattering Center (LANSCE) using a pulsed spallation neutron source. The data from four banks of detectors (±90° and ±150°) were refined by means of the Rietveld method.[13] The PC version of the General Structure Analysis System (GSAS) by Larson and Von Dreele[14] was used. Since the heavy-atom framework of $Ba_5Ga_6D_2$ was known from the single-crystal X-ray study and the structures of the two impurity phases had been determined previously,[15] all three compounds were included in the starting model. Except for some small to moderate differences in intensity, the observed and calculated histograms of the components were in good agreement. However, refinements of the phase fractions plus all three structures, or even just the $Ba_5Ga_6D_2$ structure or subsets of the positional and thermal parameters, always diverged. Therefore, the atomic positions and lattice parameters for all three phases were held fixed at the values that had been established earlier by the X-ray means in order to reduce the number of variables. The isotropic thermal parameters were still allowed to refine for all atoms in $Ba_5Ga_6D_2$. Attempts to simultaneously refine the X-ray single-crystal and neutron powder data with two different versions of the GSAS program failed, evidently because of formatting problems in the former data set.

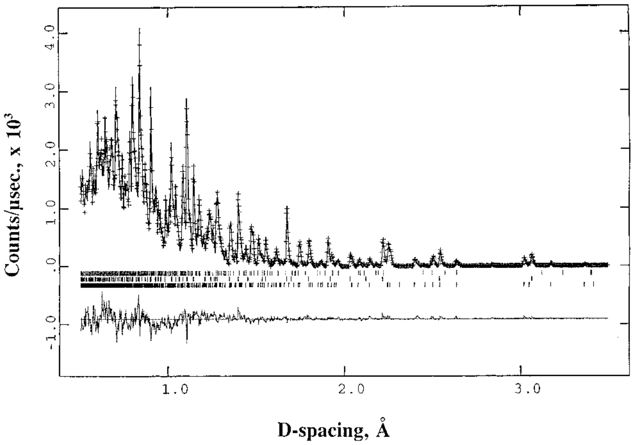

Figure 1. Histogram from the powder neutron diffraction study of $Ba_5Ga_6D_2$. The crosses mark data points, and the solid line is the refined model. The tick marks below the spectrum mark the positions of diffraction peaks of BaD_2, $BaGa_2$, and $Ba_5Ga_6D_2$, respectively. The bottom display is the difference between the experimental and calculated data.

The deuterium positions were located by alternately placing the atom on four suitable sites and allowing only the occupancy of the position to refine. After the two deuterium positions were located along 0, 0, z and $^1/_3$, $^2/_3$, z, their z coordinates, isotropic thermal parameters, and fractional occupancies were refined. The occupancies of the deuterium positions refined to within 3σ (≤8%) of 100% so they were fixed to full occupancy. The final R_p/R_{wp} indicators for the Rietveld refinement were 1.88/2.94%. Some neutron data collection parameters are listed in Table 2.

The diffraction pattern in Figure 1 shows a histogram from one of the data banks. The collected data are marked by "+" signs, and the continuous line through the data points indicates the refined spectrum. Tick marks below the spectrum indicate the reflection positions for each phase. The last row of tick marks correspond to $Ba_5Ga_6D_2$, while the first two rows pertain to BaD_2 and $BaGa_2$, respectively. The refined proportions agreed with those above. The spectrum below the tick marks of Figure 1 represents the difference between the observed and calculated intensities, on the same scale as the main spectrum. The refined spectrum fits the observed data points very well except for some deviations for small d-spacings.

Results and Discussion

Synthetic Evidence. Before the neutron diffraction study confirmed that "Ba_5Ga_6" was a dihydride, several experiments were performed that indicated hydrogen was required for the stability of the phase. Reactions of Ba (BaH_2) and Ga in welded tantalum tubes were run under two different conditions, dynamic vacuum (≤~10^{-5} Torr) and sealed within an evacuated silica jacket. Since hydrogen transports through the tantalum tubing

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(10) Sheldrick, G. M. SHELXS-86, Universität Göttingen, Germany, 1986.

(11) TEXSAN, version 6.0, Molecular Structure Corp., The Woodlands, Texas, 1990.

(12) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

(13) Rietveld, H. M. *Acta Crystallogr.* **1967**, *22*, 151.

(14) Larson, A. C.; Von Dreele, R. B. General Structure Analysis System, Report LAUR 86−748, Los Alamos National Laboratory, Los Alamos, NM, 1995.

(15) $BaGa_2$: Bruzzone, G. *Bull. Sci. Fac. Chim. Industr. Bologna* **1966**, *24*, 113. BaH_2: Bronger, W.; Chi-Chien, S.; Müller, P. *Z. Anorg. Allg. Chem.* **1987**, *545*, 69. Ba_8Ga_7: Fornasini, M. L. *Acta Crystallogr.* **1983**, *39C*, 943.

Table 3. Positional and Isotropic Thermal Parameters for $Ba_5Ga_6H_2$[a]

atom	Wyckoff	x	y	z	B_{eq},[b,c] (Å^2)
Ba1	6*d*	0.0244(1)	0.3339(2)	0.2621(2)	1.37(1)
Ba2	2*a*	0	0	0.03204(9)	1.88(3)
Ba3	2*b*	$^1/_3$	$^2/_3$	0	0.86(2)
Ga1	6*d*	0.4721(3)	0.3499(3)	0.0890(2)	1.44(5)
Ga2	6*d*	0.4615(3)	0.3200(3)	0.4335(1)	1.30(5)
D1	2*b*	$^1/_3$	$^2/_3$	0.318(2)	4.3(4)
D2	2*a*	0	0	0.220(1)	1.3(1)

[a] Heavy atom positions and thermal ellipsoids are from X-ray refinement; the deuterium parameters come from neutron diffraction. [b] $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\vec{a}_i\vec{a}_j$ for X-ray data. [c] Refined B values for the heavy atoms from neutron diffraction were 1.14(6), 0.08(1), 2.2(2), 1.7(1), and 0.31(6), respectively.

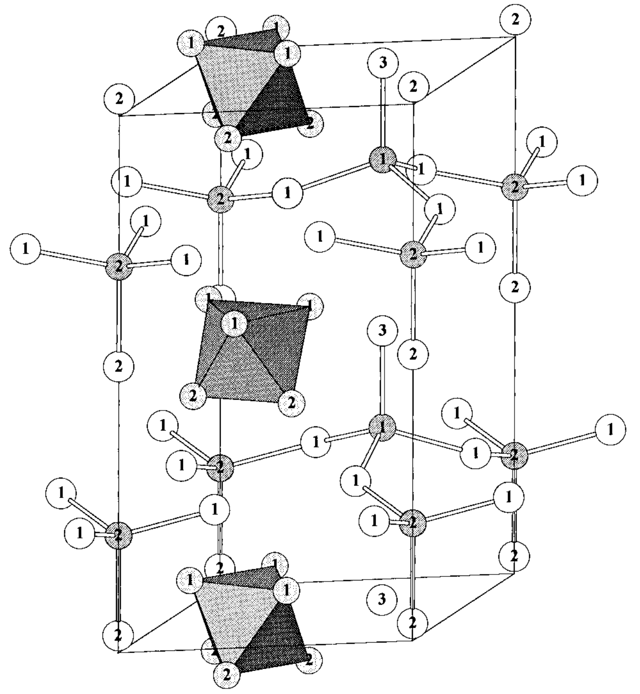

Figure 2. Unit cell of $Ba_5Ga_6(H,D)_2$. Gallium atoms (shaded) define isolated trigonal antiprisms that are surrounded by barium cations (open circles). The deuterium atoms (isolated shaded circles) lie in two different tetrahedral holes formed by barium.

at or above ~550 °C, the hydrogen is lost from heated containers under dynamic vacuum. As in many systems,[5,6] all reactions performed under an active vacuum produced only known binary compounds, $BaGa_2$ and Ba_8Ga_7 in this instance.[15] Conversely, the title phase was always formed from barium, gallium, and barium hydride when the Ta container was held within an evacuated and sealed silica jacket. Distilled Ba used as received was sufficient to provide good amounts of $Ba_5Ga_6H_2$ since such Ba reagents usually contain at least 10−20 at. % H.[5,7] In any case, the earlier lack of single phase $Ba_5Ga_6H_2$ precluded corroborative property measurements. Although fluoride provides a good stand-in for fluoride in many other instances,[5,6] we were unable to obtain $Ba_5Ga_6F_2$.

Structural Characterization. The combined positional and isotropic thermal data for $Ba_5Ga_6(H,D)_2$ are given in Table 3. The primary structural feature is the isolated Ga_6 octahedra solvated by barium cations, as illustrated for the cell contents in Figure 2. The bond distances within the octahedra range from 2.671(3) Å (Ga2−Ga2) to 2.743(4) Å (Ga1−Ga1) (Table 4) and are typical for gallium clusters.[16] The barium cations lie over all of the edges of the octahedron at distances of 3.387(2)−3.548(3) Å, Figure 3. The large barium atoms also create several tetrahedral voids that are suitable for hydrogen (deuterium) anions. The deuterium atom labeled D1 is in the center of the more regular tetrahedron with Ba3 (2.62(2) Å) and 3 Ba1 (2.624(7) Å) neighbors, Figure 4. The D2 atom in contrast is slightly closer to three Ba1 atoms at 2.576(4) Å while the fourth Ba2 atom is farther away, 2.71(2) Å. The averages are 2.62 and 2.61 Å, respectively.

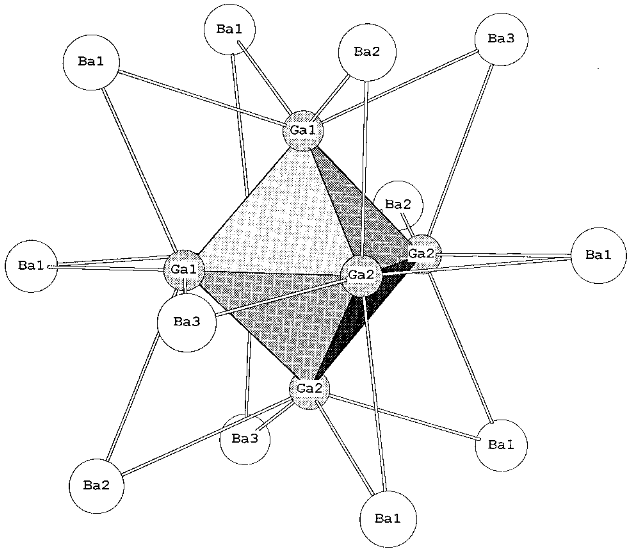

Figure 3. The gallium octahedron and its barium neighbors.

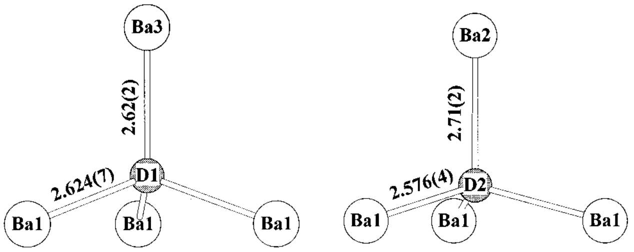

Figure 4. Coordination environments around the deuterium atoms, with the 3-fold axes vertical.

The original space group reported for the pseudo binary phase Ba_5Ga_6 was $P\bar{6}c2$ (No. 188), but this required the Ba2 atom to be split between two positions. It also forced all tetrahedral barium cavities in the structure to have equal dimensions. Refinement in space group $P\bar{3}c1$ removes the split position and provides two cavities of suitable size. This is significant because there are four tetrahedral holes in the structure, and only two are necessary to accommodate the amount of hydrogen for two formula units. The two unoccupied tetrahedral sites are larger and share common bases with the occupied pair of tetrahedra, Figure 2. Those adjacent to D1 and D2 would (without contraction on occupation) provide average Ba−D distances that are 0.09 and 0.14 Å larger than the filled sites, respectively. The shorter Ba−D distances in BaD_2 are 2.57 and 2.61 Å,[15] so it is reasonable that deuterium occupies the smaller pair of tetrahedra in $Ba_5Ga_6H_2$ with 2.61 and 2.62 Å average distances. There are still other cavities in the unit cell that are large enough for deuterium (hydrogen), but they have gallium in the coordination polyhedron, which would be unfavorable.

Comparison of the heavy-atom coordinates in this refinement with the positions reported before for Ba_5Ga_6[2] show only small deviations in the third decimal place for barium. The main differences originate with the change in space group assignment.

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(16) Belin, C.; Tillard-Charbonnel, M. *Prog. Solid State Chem.* **1993**, *22*, 59.

Table 4. Selected Bond Distances in $Ba_6Ga_5H_2$ and $Ba_5Ga_6D_2$ (Å)[a]

Ga1−Ga1	2×	2.743(4)	Ba1−D2		2.576(4)	Ba3−D1		2.62(2)
Ga1−Ga2		2.720(2)	Ba1−D1		2.624(7)	Ba3−Ga1	3×	3.394(2)
Ga1−Ga2		2.736(3)	Ba1−Ga2		3.387(2)	Ba3−Ga2	3×	3.442(2)
Ga1−Ba3		3.394(2)	Ba1−Ga1		3.393(3)	Ba3−Ba1	3×	4.239(2)
Ga1−Ba1		3.393(3)	Ba1−Ga2		3.511(3)			
Ga1−Ba2		3.394(2)	Ba1−Ga1		3.548(3)	D1−Ba3		2.62(2)
Ga1−Ba1		3.548(3)	Ba1−Ba2		4.152(2)	D1−Ba1	3×	2.624(7)
			Ba1−Ba3		4.239(2)			
Ga2−Ga2	2×	2.671(3)	Ba1−Ba1	2×	4.327(2)	D2−Ba1	3×	2.576(4)
Ga2−Ga1		2.720(2)	Ba1−Ba1	2×	4.339(2)	D2−Ba2		2.71(2)
Ga2−Ga1		2.736(3)						
Ga2−Ba1		3.387(2)	Ba2−D2		2.71(2)			
Ga2−Ba3		3.442(2)	Ba2−Ga1	3×	3.394(2)			
Ga2−Ba2		3.485(2)	Ba2−Ga	3×	3.485(2)			
Ga2−Ba1		3.511(3)	Ba2−Ba1	3×	4.152(2)			

[a] Heavy-atom distances from X-ray study; deuterium separations from combined X-ray and neutron results.

The single (split) gallium position in the previous structure corresponds to two different sites in the current refinement. This reduces the cluster symmetry to D_3, an elongated and slightly twisted trigonal antiprism with a 0.072(5) Å range in edge distances.

As pointed out to us by a reviewer, the pattern of shared Ba_4H tetrahedron in $Ba_5Ga_6H_2$ is the same as in sheet silicates of formula $Si_2O_5^{2-}$ in which alternate tetrahedra point in opposite directions. However, we have been unable to find any nominally isotypic ASi_2O_5 phases, possibly because of the large cluster counterion here.

The $Ba_5Ga_6H_2$ compound represents a novel convergence of naked cluster chemistry, the effects of what was originally impurity hydrogen, and Zintl phase concepts. Isolated "naked" clusters are relatively rare for gallium, other examples presently being limited to tetrahedra in $Ca_{11}Ga_7$[17] and to two hypoelectronic examples, Ga_{11}^{7-} ($\sim D_{3h}$) in Cs_8Ga_{11} and the centered $Ga_{10}Ni^{10-}$ ($\sim C_{3v}$) in $Na_{10}Ga_{10}Ni$.[18] However, an increasing variety of such clusters is known for indium and, especially, thallium,[19] including the O_h version Tl_6^{8-} in $Na_{14}K_6(Tl_6)Tl_{12}M$ phases (M = Mg, Zn, Cd, Hg)[20] and tetragonally compressed Tl_6^{6-} in KTl and CsTl.[21] The ion Ga_6^{8-} is, of course, a member of a polyhedra family with skeletal electron-count−geometry relationships that fit into the classic Wade's rule description, $2n + 2 = 14$ (p) electrons for bonding in this case. Surprisingly, compounds containing many of these clusters also exhibit structures with evidently only closed-shell electronic states and thus qualify as Zintl (valence) phases.[4] Finally, the pervasive presence of hydrogen impurities in commercial alkaline-earth metals (and some other divalent metal products as well) means many supposedly simpler compounds of these, especially with post-transition (*p*) elements it appears, are in fact hydrides. We have found that many structural families exhibit these impurity effects, Mn_5Si_3-, Yb_5Sb_3-, and Cr_5B_3-types for example, as well as isolated examples for other compounds.[6,22] Future publications will detail these results.

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Supporting Information Available: Tables of further X-ray data collection and refinement information and the anisotropic displacement parameters for the heavy atoms (2 pages). Ordering information is given on any current masthead page.

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(17) Fornasini, M. L.; Merlo, F. *Z. Kristallog.* **1989**, *187*, 111.

(18) Henning, R. W.; Corbett, J. D. To be submitted for publication.

(19) Corbett, J. D. In *Chemistry, Structure and Bonding in Zintl Phases and Ions*; Kauzlarich, S., Ed.; VCH: New York, 1996; Chapter 3.

(20) Dong, Z.-C.; Corbett, J. D. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1006.

(21) Dong, Z.-C.; Corbett, J. D. *Inorg. Chem.* **1994**, *35*, 2301.

(22) Leon-Escamilla, E. A.; Huang, B.; Corbett, J. D. To be published.