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Two New Cluster Ions, $Ga[GaH_3]_4^{5-}$ with a Neopentane Structure in $Rb_8Ga_5H_{15}$ and $[GaH_2]_n^{n-}$ with a Polyethylene Structure in $Rb_n(GaH_2)_n$, Represent a New Class of Compounds with Direct Ga−Ga Bonds Mimicking Common Hydrocarbons

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S *Supporting Information*

ABSTRACT: The first examples of a new class of gallium hydride clusters with direct Ga−Ga bonds and common hydrocarbon structures are reported. Neutron powder diffraction was used to find a $Ga[GaH_3]_4^{5-}$ cluster ion with a neopentane structure in a novel cubic structure type of $Rb_8Ga_5H_{15}$. Another cluster ion with a polyethylene structure, $[GaH_2]_n^{n-}$, was found in a second novel $(RbGaH_2)_n$ hydride. These hydrocarbon-like clusters in gallium hydride materials have significant implications for the discovery of hydrides for hydrogen storage as well as for interesting electronic properties.

Aluminum clusters have recently been predicted to have favorable properties for hydrogen storage[1−3] but are unfortunately impractical to synthesize. In contrast, gallium is known to form several clusters in the presence of alkali metals.[4,5] Given the close chemical similarity between aluminum and gallium, we began a program of synthesis of gallium hydrido clusters by sintering gallium in the presence of alkali metals under hydrogen at elevated temperatures. The principal objective of the research was to gain knowledge of any new cluster geometries that could be transferred to possible aluminum- or boron-containing analogues. Our initial approach was to avoid a two-step process involving first making and then hydriding the gallium cluster, as a more practical and robust hydrogen storage system would be achieved if the metals could react directly with hydrogen and form a hydrogen storage compound.

A successful screening search was performed with varied reaction conditions. Gallium was mixed with different alkali metals in a mortar and then pelletized. The starting materials used were obtained from Alfa Aesar and ABCR. Pellets were placed in aluminum oxide tubes and inserted into stainless steel tube reactors. The reactors were pressurized with 5 MPa hydrogen gas and heated in a tube furnace to a temperature of 573 K. The temperature was monitored using stainless steel-encapsulated thermocouples inserted in the aluminum oxide tubes. The reactors were heated overnight and then cooled to room temperature, after which the samples were extracted. All sample handling was performed under an inert argon atmosphere in a glovebox to avoid oxidation of the chemicals. The reaction products were analyzed using a Panalytical X'pert Pro powder diffractometer with monochromatic Cu Kα1 radiation (λ = 1.540598 Å) and a germanium monochromator. The obtained diffraction patterns were analyzed and compared with known phases from the JCPDF database.[6]

Table 1. Atomic Positions in $Rb_8Ga_5D_{15}$

atom	Wyckoff	*x*/*a*	*y*/*b*	*z*/*c*
Rb1	16c	0	0	0
Rb2	48f	0.7985(1)	1/8	1/8
Ga1	32e	0.20955(6)	0.20955(6)	0.20955(6)
Ga2	8a	1/8	1/8	1/8
D1	96g	0.45023(9)	0.1920(3)	0.5357(3)
D2	16d	1/2	1/2	1/2
D3	8b	5/8	5/8	5/8

With the alkali metals Li, Na, and K, no new materials were formed; only previously known binary and ternary intermetallic hydrides were synthesized. However, with the larger alkali metals Rb and Cs, new phases were observed in the X-ray diffraction (XRD) patterns recorded from the end products.

For the rubidium compounds, when the Rb/Ga ratio was 8:5, a white, almost single-phase powder sample was indexed to a large cubic unit cell using TREOR in Panalytical Highscore Plus and assigned to the space group $Fd3\overline{m}$ (No. 227) for $Rb_8Ga_5H_{15}$. The metal structure was solved using JANA 2006[7] together with EXPO2004[8] using direct methods. Impurities of the alkaline binary hydrides were included in the refinements. Similar diffraction data were observed for cesium, although pure single phases were difficult to obtain; that work will be the subject of a future publication.

The hydrogen positions were determined by neutron diffraction at room temperature using deuterated samples at the time-of-flight powder diffractometer GEM at ISIS for $Rb_8Ga_5D_{15}$. In order to refine the deuterium positions, the space group had to be changed to $Fd\overline{3}$ (No. 203) for $Rb_8Ga_5D_{15}$, with a cubic cell

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Figure 1. $Ga(GaH_3)_4^{5-}$ cluster ion with a neopentane structure. At room temperature, very elongated thermal ellipsoids for the deuterium atoms indicate a significant librational motion of the GaH_3 units around the Ga−Ga bond. The view down the Ga−Ga bond shows that the GaH_3 unit is rotated ~11° from the Ga−Ga angle in the cluster.

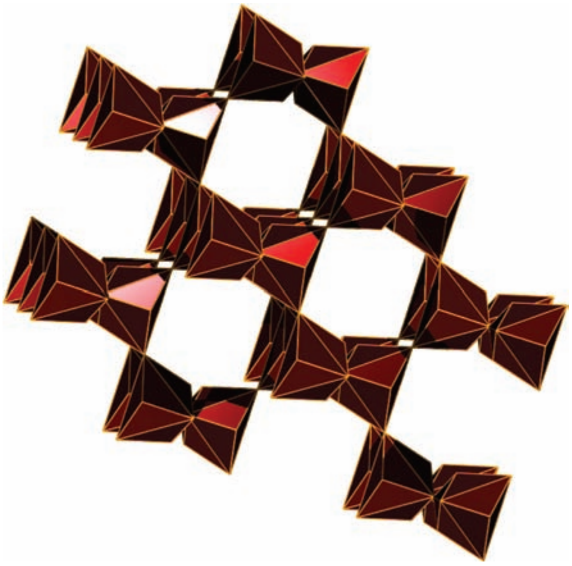

Figure 2. Three-dimensional network of $Rb_2Ga(GaH_3)^{3-}$ units connected by sharing of the Rb atoms.

parameter (a) of 16.7852(8) Å for the hydride and 16.7632(1) Å for the deuteride. The initial deuterium positions were found using FOX,[9] and the full structure was refined using GSAS[10] ($R_p = 0.0181$, $R_{wp} = 0.0201$, and $\chi^2 = 5.882$; see Table 1).

The most prominent feature of the new structure was a hitherto unknown $Ga(GaH_3)_4$ cluster with a neopentane $[C(CH_3)_4]$ molecular structure (Figure 1), in contrast to the usual alanate (AlH_4^-) and gallate (GaH_4^-) ions, which have a methane (CH_4)-like structure. A simple electron count for the $Ga(GaH_3)_4$ cluster gave a charge of −5. The Ga−Ga−Ga angle is fixed at the ideal tetrahedral angle from the space-group symmetry, but the H−Ga−H angle between the terminal hydrogen atoms is slightly smaller, probably as a consequence of space constraints.[11] All of the terminal hydrogen atoms were refined in the same symmetry-equivalent 96-fold site. Each symmetric tetrahedron of gallium atoms is described by two positions: the central Ga atom sits on an 8-fold site, while the outer Ga atoms sit on 32-fold sites. Each tetrahedron is face-capped by two Rb ions sitting on 16-fold sites, giving a $[Rb_2[Ga(GaH_3)_4]^{3-}$ entity. These two Rb atoms are, however, also shared by the neighboring units, forming a three-dimensional network as depicted in Figure 2. This network is integrated into a framework having a local structure related to the corresponding binary alkali hydrides. Ordinary binary alkali hydrides, including RbH, have the NaCl-type structure, which can be viewed as either edge-sharing RbH_6 or HRb_6 octahedra. In the new compound, the $[Rb_2[Ga(GaH_3)_4]^{3-}$ motif is embedded in a

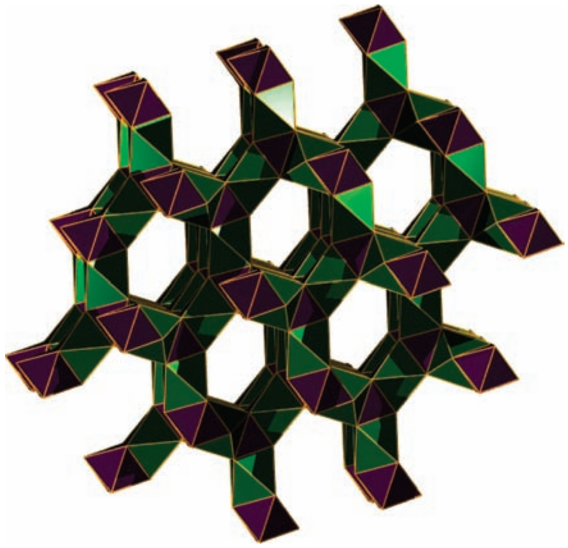

Figure 3. Network with open channels formed by the other Rb atoms in the 48f sites, consisting of face-sharing HRb_6 octahedra. One type of octahedron is true (lilac) and the other two are slightly distorted (green).

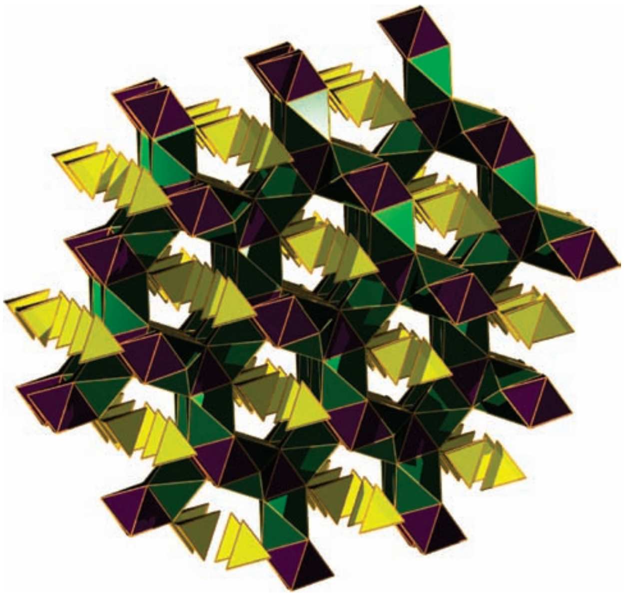

Figure 4. Illustration of the two integrated networks, showing how the $Rb_2Ga(GaH_3)^{3-}$ networks fill the RbH channels. For clarity, the face-capping Rb atoms and the terminal H atoms have been eliminated.

Table 2. Atomic Positions in $(RbGaD_2)_n$

atom	Wyckoff	x/a	y/b	z/c
Rb	4c	0.3828(3)	1/4	0.1734(3)
Ga	4c	0.4365(3)	1/4	0.5351(2)
D1	4c	0.2229(4)	1/4	0.4822(3)
D2	4c	0.6044(4)	1/4	0.7056(3)

network of face-sharing HRb_6 octahedra consisting of one true octahedron and two slightly distorted octahedra, forming a combined (RbH) and Rb^+ network (Figure 3)

All of the alkali metal atoms in this network are described with a common 48-fold site, and the two hydrogen positions are described with 8- and 16-fold sites corresponding to the true and distorted octahedra, respectively. This means that the alkali metal cations in the 48-fold sites act as counterions to both to the interstitial hydride ions and the $[Rb_2[Ga(GaH_3)_4]]^{3-}$ network.

In Figure 4, the RbH network can also be seen to form channels in which the $[Rb_2[Ga(GaH_3)_4]]^{3-}$ units are intercalated. This implies a rather intriguing bonding. The total structure of $Rb_8Ga_5H_{15}$ can be described as $(RbH)_2(RbH)[(Rb^+)_3[Rb_2[Ga(GaH_3)_4)]^{3-}]$. During the neutron data refinement, we found that although there was no residual scattering density, the profile fit was still poor. Refining the anisotropic temperature parameters for the deuteride ions at the 96-fold positions gave a much better fit, with the R_F value decreasing by a factor of 4. When the shape of thermal ellipsoids was analyzed, it was concluded that already at room temperature the deuterium atoms associated with the gallium complex were strongly librating but may also have contained a static distortion (Figure 1) The terminal deuterium positions could also be refined in a 192-fold site with half occupancy in an attempt to better describe any static distortion. The R_F value did not show any significant decrease, and the deuterium atoms still showed significant anisotropic displacement behavior that is most likely indicative of a very flexible $Ga(GaD_3)_4$ cluster rather than a static distortion. However, the possibility of a static distortion cannot be ruled out. A similar librational motion has also been observed by quasielastic neutron scattering in solid neopentane, suggesting further similarities with the corresponding hydrocarbons, and indeed, this technique could be used to study further the details of the motion of the cluster.[12]

When the anisotropic temperature parameters of the other atoms were allowed to be refined, no significant deviations were observed from the refined isotropic temperature parameters, indicating that most of the dynamic motion is associated with the terminal hydrogen atoms on the cluster.

At a Rb/Ga ratio of 1:1, the indexing of the corresponding XRD patterns indicated the space group *Pnma* (No. 62) for $(RbGaH_2)_n$. For $(RbGaD_2)_n$, the PUS diffractometer at the JEEP2 reactor at Kjeller, Norway, was used with a neutron wavelength of 1.5556 Å. $(RbGaH_2)_n$ was refined with the cell parameters $a = 7.4751(1)$ Å, $b = 4.4905(1)$ Å, and $c = 9.5626(1)$ Å for the hydride and $a = 7.4536(4)$ Å, $b = 4.4838(2)$ Å, $c = 9.5466(4)$ Å for the deuteride. The refinement of the diffraction pattern was done using the same procedure as for $Rb_8Ga_5D_{15}$, giving final agreement factors $R_{wp} = 0.120$, $R_p = 0.121$, and $\chi^2 = 1.66$ (see Table 2).

The structure is characterized by negatively charged one-dimensional infinite gallium−hydrogen chains with a polyethylene structure counterbalanced by interlayers of Rb counterions, as depicted in Figure 5. The Ga−Ga and Ga−H bonds in the chains are slightly longer than the corresponding bonds in the neopentane cluster, indicating that the RbH framework in the latter hydride probably exerts a compression on the cluster.

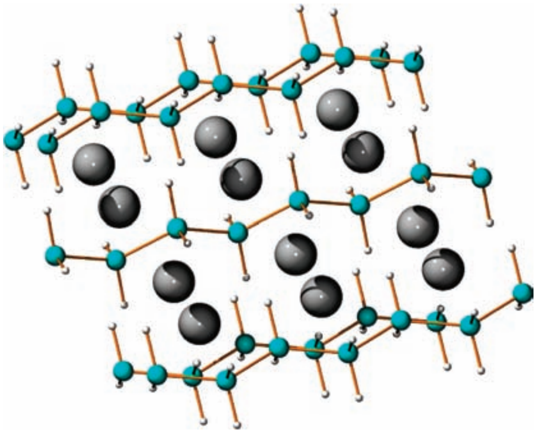

Figure 5. Linear $(GaH_2)_n^{n-}$ chains intercalated by Rb atoms.

These are the first gallium−hydrogen clusters with direct gallium−gallium bonds forming rather common hydrocarbon-like structures, implying that further substitutions of hydrogen atoms with GaH_3 units or vice versa or variations of the alkali to gallium ratio could result in a variety of new compositions and molecular architectures. Aluminum and gallium have much in common, and if similar aluminum-based compounds can be found, then there could be a significant impact on hydrogen storage. Several intermetallics containing both aluminum and gallium that also include alkali metals have been found.[13−15] The clusters have in themselves high hydrogen contents but can also be seen as intermediates in the formation of conventional alanates or gallanates according to the following equations:

$$(AAlH_2)_5 + H_2 \rightleftarrows A_5Al_5H_{12} + 4H_2 \rightleftarrows 5AAlH_4$$

where A is an alkali metal.

Any cluster with direct metal−metal bonds could be a possible intermediate in the hydrogenation of hydrides based on BH_4^-, AlH_4^-, and GaH_4^- ions. Indeed, there has been a long search for an intermediate in the hydrogenation/dehydrogenation mechanism, which has been shown experimentally to be promoted by titanium doping, although the mechanism is still not understood.[16]

No hydrocarbon-similar hydrido clusters with direct metal−metal bonds have been found until now for any of the group III metals, which may be a consequence of the difficulty in obtaining well-crystallized compounds. There has, however, been computational work on this type of cluster (e.g., $Ga_2H_2^{2-}$, $Ga_2H_4^{2-}$, $Ga_2H_6^{2-}$, etc.), where the strength of the Ga−Ga bond has been discussed in relation to corresponding single and multiple C−C bonds.[17,18] In our new clusters, the Ga−Ga bond length is between those of a single bond and a double bond when compared with the computations. The colors show that the electrons are well-localized as in covalent hydrocarbons, and the bond angles indicate simple sp^3 hybridization, which further implies that the bonding in these hydrocarbon-like clusters is relatively straightforward.

The similarity with hydrocarbon structures may also open up the possibility of doping the new compounds with group IV elements or vice versa, which could lead to interesting electric properties. In the somewhat related series $BaAl_2H_2$/BaAlSiH/$BaSi_2$, which is of interest for superconductivity, the continuous substitution of an Al−H entity with a Si lone pair could shift the electric conductivities to promote a semiconductor−semimetal transition.[19]

ASSOCIATED CONTENT

Ⓢ Supporting Information. Tables with atomic positions and displacement parameters, tables of interatomic distances and angles, and CIF files for $Rb_8Ga_5D_{15}$ and $(RbGaD_2)_n$. This material is available free of charge via the Internet at http://pubs.acs.org.

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