

Coordination Preference of Ga in Hydrides

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Aluminum and gallium show some interesting differences in their coordination chemistry. Solid GaH₃ is unknown, in contrast to solid AlH₃. Ga equivalents of Li₃AlH₆, Na₃AlH₆, and other hydrides whose structure contain AlH₆³⁻ ions, are unknown. We relate these differences to an instability of the hexacoordinated gallium moiety.

1. Introduction

Contrary to what one would expect from general periodic trends, gallium has very similar atomic radii¹ to aluminum and has a higher electronegativity.^{2,3} The transition-metal contraction³ may partially explain these features, in analogy to the lanthanide contraction⁴ responsible for the extremely similar properties of, for example, zirconium and hafnium.

Periodic analogy is a prominent part of inorganic-chemical thinking, and hence, the chemist may easily assume too great of a similarity between members of a given group. In the present contribution, we will focus on certain differences between Al and Ga hydrides, illustrated by band-structure, solid-state, and molecular quantum-chemical calculations, as well as literature data.

Molecular hydrides of Al and Ga have been widely studied because of their use in chemical vapor deposition (CVD) technology.^{5–9} The simple molecules AlH₃ and GaH₃ are electron deficient but are frequently observed in the vapor

phase. In the dimeric molecules Al₂H₆^{10–12} and Ga₂H₆,^{12–14} the metal atoms share two of the hydrogen atoms such that both of them gain four-fold quasitetrahedral coordination in structures that qualitatively resemble diborane (B₂H₆).¹⁵ Larger oligomers or clusters of the form Al_nH_{3n}¹¹ (*n* = 3, 4) have also been reported and are in fact predicted by theory to be more stable than AlH₃.¹⁶ Other molecular aluminum hydrides have also been reported,^{10,14,17} the most important being AlH, AlH₂, and Al₂H₄.

Both Al and Ga form ternary hydrides with alkali and alkaline earth metals. Such ternary hydrides have been the subject of intensive research because of their possible use as hydrogen-storage materials.¹⁸ MAIH₄ and MGaH₄ have been synthesized and characterized for several alkali metals, M. On the other hand, M₃AlH₆ compounds have been reported for a number of M constituents, while analogous ternary gallium hydrides have remained hypothetical.

The present contribution attempts to explain some aspects of the coordination preferences of Al versus Ga on the basis of computational results. Calculated structures of the types MAIH₅ and MGaH₅, in which M is an alkaline earth metal, and molecular quantum-chemical results for the free ions AlH₄⁻, GaH₄⁻, AlH₆³⁻, and GaH₆³⁻ will be presented.

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2. Computational Details

Band-structure calculations were performed using the VASP program package.¹⁹ The PAW scheme²⁰ was used throughout, with an energy cutoff parameter of 500 eV. The PBE density functional^{21,22} was employed. In the geometry optimizations, all degrees of freedom were relaxed, including the unit-cell parameters. The force convergence criterion was set to 4 meV Å⁻¹, while SCF convergence was considered to be achieved at an energy difference between successive iterations of less than 10⁻⁷ eV. Gaussian smearing of the electronic occupations was used with a standard deviation of 0.2 eV.

To maximize the probability of finding global energy minima, we started the geometry optimizations from the same fifty different trial structures used in the previous work²³ on MgAlH₅ and BaAlH₅. Structural data for these and other structures were taken from the ICSD database.²⁴ After the initial screening was complete, the most stable candidate structures underwent further optimization with a denser grid of k points. In the literature, Monkhorst meshes²⁵ have been extensively employed for generating k points for integration over reciprocal space. Such meshes are incompatible with certain symmetries and may lead to artificial results in the geometry optimizations. Hence, they were not used in the present calculations. Instead, γ -centered k-point meshes were generated using

$$\chi_i = \left[\frac{\rho_N}{N} \right]^{1/3} \frac{|\vec{a}_i|}{V_r^{1/3}}, \quad (1)$$

where $i = 0, 1, 2$, denoting the three reciprocal directions, χ_i is the number of k points in the reciprocal direction i , ρ_N is a density constant in units of k-point atoms, \vec{a}_i is a reciprocal lattice vector, N is the number of atoms in the unit cell, and V_r is the volume of the reciprocal cell. A value of 1050 k-point atoms were used for ρ_N , and the values of χ_i were rounded to the nearest integer. Other rounding schemes can be employed, but they were not used in this work.

This scheme gives a k-point density that depends on the number of atoms, giving similar descriptions for different volumes of the unit cell. For the final energy calculations, in which only negligible changes in geometries were anticipated, the k points were generated using

$$\chi_i = [\rho_V]^{1/3} |\vec{a}_i|, \quad (2)$$

where 15 000 k-point Å³ was used for the density constant ρ_V . Because only negligible changes in volume were expected, the volume density was considered to be the better choice.

Molecular calculations were performed with the Gaussian 03 package.²⁶ The different methodological approaches used are listed in Table 1, and references can be found on the Gaussian web site.²⁷ Geometry optimizations were carried out under T_d (tetrahydrides) or O_h (hexahydrides) symmetry restrictions for all methods. For CCSD(T), only single-point energy calculations were performed,

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Table 1. Difference Between the Decomposition Energies for GaH₆³⁻ and AlH₆³⁻ (ΔE) as Calculated with Different Methods^a

method	ΔE (kJ mol ⁻¹)
B3LYP/6-311++G**	47.3
B3LYP/6-311++G(3df, 3pd)	38.5
MP2/6-311++G**	55.6
HF/6-311++G**	56.1
CCSD(T)/6-311++G(3df, 3pd) ^b	28.5

^a The positive numbers signal that AlH₆³⁻ is more stable than GaH₆³⁻.
^b Geometry from B3LYP/6-311++G(3df, 3pd) calculations.

using geometries from B3LYP/6-311++G(3df, 3pd) calculations. The very large basis sets were deemed necessary because of the strong anionic charge on the species under study, and B3LYP results for two different basis set sizes indicate that the basis is reasonably saturated. Vibrational spectra were calculated, and for the tetrahydrides, the optimized structures represent true local minima as witnessed by the absence of imaginary frequencies in the spectra. The hexahydrides showed two degenerate imaginary frequencies of E_g symmetry. Test optimizations with D_{4h} instead of O_h symmetry converged toward dissociation into two hydride ions. Unsurprisingly, the resulting plane quadratic tetrahydride ion shows imaginary frequencies corresponding to internal coordinates leading to tetrahedral structures.

3. Results and Discussion

No member of the series MGAH₅ (M = Be, Mg, Ca, Sr, and Ba) has, to our knowledge, hitherto been synthesized and may never be for reasons detailed below. Energy minimizations were performed, and the most stable structure for each of these hydrides is shown in Figure 1. All structures include isolated GaH₄⁻ complexes, in striking difference to the aluminum analogues studied in previous works,^{23,28} which all exhibit octahedral AlH₆³⁻ complex units arranged in chains. In BeAlH₅, the anions form²AlH₄⁻ planes with corner-sharing octahedra, while the others with corner-sharing octahedra are arranged in¹AlH₅²⁻ chains. In the structural arrangements of the gallium compounds, one hydrogen atom per formula unit is not bonded to Ga, but rather, it is bound to the alkaline earth constituent atoms. In the following, these hydride ions will be referred to as isolated ionic hydrogen atoms (IHs). The coordination of the IHs varies throughout the series. For M = Be, Mg, and Ca, the IHs are shared between the MH_n polyhedra, while the

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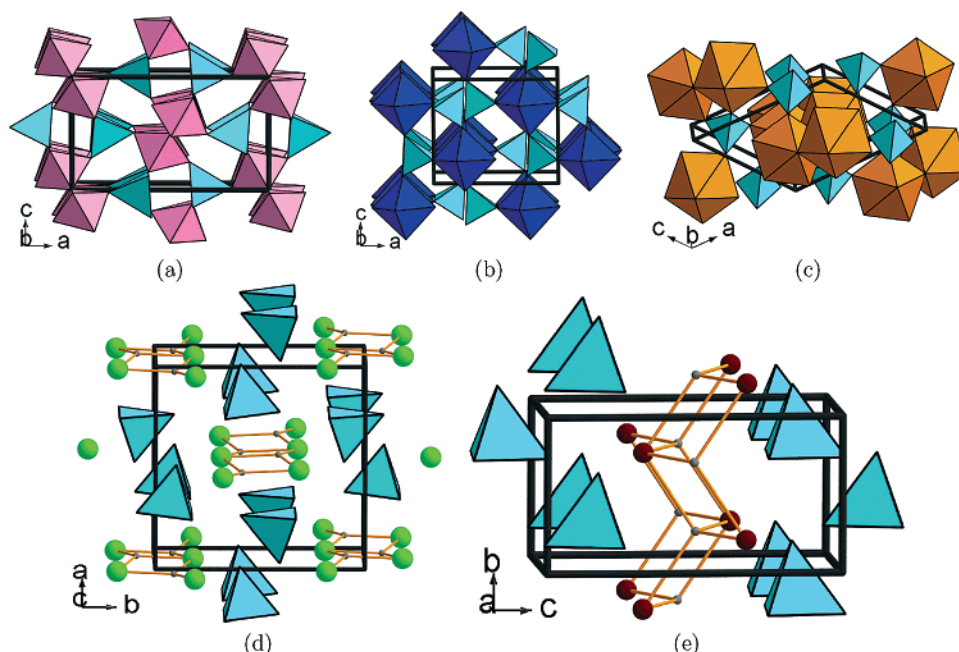


Figure 1. Computationally derived hypothetical crystal structures of (a) BeGaH₅, (b) MgGaH₅, (c) CaGaH₅, (d) SrGaH₅, and (e) BaGaH₅: GaH₄ tetrahedra, light blue; BeH₄ tetrahedra, pink; MgH₆ octahedra, dark blue; capped CaH₇ octahedra, orange; Sr, green spheres; Ba, red spheres. The isolated ionic hydrogen atoms (IHs) are shown by small spheres.

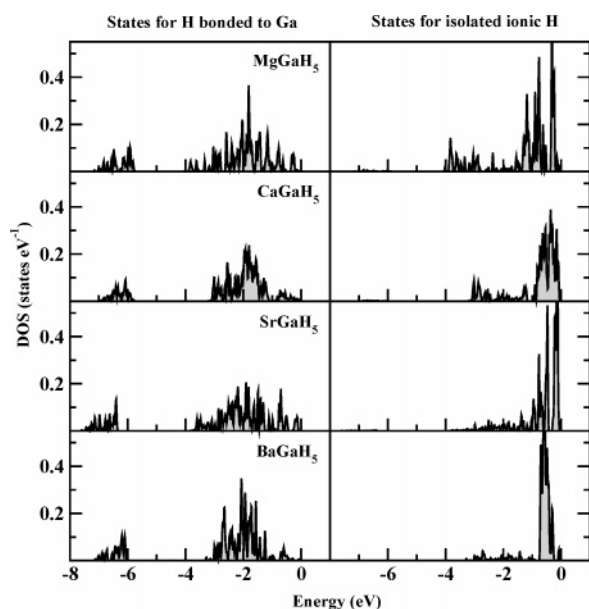


Figure 2. Site-projected DOS for H bonded to Ga, and for isolated ionic hydrogen (IH). All lines mark *s* states. The IH atoms are seen to be the energetically least stable and exhibit the most ionic characteristics. The ionicity increases with the increasing atomic number of the alkaline earth constituent.

IHs should be regarded as separate coordination ingredients in SrGaH₅ and BaGaH₅.

The site-projected density-of-states (DOS) profiles (Figure 2) for the regular bonds and IHs are compared for all the compounds subject to study. The illustrations convey that the IHs are more weakly bonded than the H atoms coordinated to the gallium atoms and that they exhibit stronger ionic character than the complex bonded hydrogen atoms. We have carried out geometry optimizations of the hypothetical structure for the Mg(GaH₄)₂ phase starting from the

structure of Mg(AlH₄)₂ established by Fichtner et al.²⁹ and later reproduced theoretically by Løvvik and Molin.³⁰ The calculated reaction energy for the decomposition reaction $2\text{MgGaH}_5 \rightleftharpoons \text{Mg}(\text{GaH}_4)_2 + \text{MgH}_2$ gave a value of -16 kJ mol^{-1} , in contrast to the 5 kJ mol^{-1} value reported²³ for the aluminum analogue, which points to a lower stability of MgGaH₅. Correspondingly, optimizations were performed for Ca(AlH₄)₂ and Ca(GaH₄)₂, in both cases using structural data for the Ca(AlH₄)₂ compound first reported by Løvvik.³¹ This resulted in -34 and 52 kJ mol^{-1} for the hypothetical decomposition of the hypothetical hydrides CaGaH₅ and CaAlH₅, respectively. These reactions have been chosen as illustrations because they do not include any change in oxidation state for any of the atoms. This allows for greater accuracy in the results because of cancellation of errors.

From the DOS profiles in Figure 2, one would assume that the lower stability for MgGaH₅ may be attributed to the instability of the IH features of the material. Further, the calculated reaction energies for the reactions $\text{NaM}'\text{H}_4 + 2\text{NaH} \rightleftharpoons \text{Na}_3\text{M}'\text{H}_6$, with $\text{M}' = \text{Al}$ and Ga, are as -17 and $+80 \text{ kJ mol}^{-1}$, respectively. In this case, the optimizations of both Na₃M'H₆ structures were started from the Na₃AlH₆ structure, forcing Ga to assume octahedral coordination. The latter constraint obviously results in a very unstable system. The results so far indicate that gallium hydrogen complexes strongly prefer tetrahedral coordination over octahedral, while aluminum may assume any of the two arrangements.

To further elucidate the qualitative differences between the coordination preferences of $\text{M}' = \text{Al}$ and Ga, quantum chemical calculations were performed for the tetrahedral M'

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H_4^- and octahedral MH_6^{3-} complexes of both metals. The $\text{MH}_6^{3-} \rightleftharpoons \text{MH}_4^- + 2\text{H}^-$ reaction can serve as a test for the relative stability of the hexahydride complex versus the tetrahydride complex. The absolute energy for these reactions range from -1067 to -1180 kJ mol^{-1} , depending on the metal and the chosen computational procedure. However, the absolute values are not particularly interesting in the present context, since a relatively small ion with a charge of $3-$ will be highly unstable in vacuum, for obvious reasons of electrostatic origin. Nevertheless, molecular calculations allow us to isolate factors that are of local character and rely solely on the differences in atomic properties.

The differences in the decomposition energy (ΔE) between AlH_6^{3-} and GaH_6^{3-} thus obtained are listed in Table 1. In each case, ΔE for Al is the smallest, resulting in the conclusion is that AlH_6^{3-} is more stable than GaH_6^{3-} . The good agreement between the results obtained by the different computational methods is gratifying. While we would not like to draw any firm conclusions solely on the basis of the molecular results, they fail to disprove the hypothesis that gallium has a stronger preference for tetrahedral coordination than aluminum.

Turning our attention to solid crystalline hydrides of aluminum and gallium, we note that the crystal structure $\alpha\text{-AlH}_3$ comprises AlH_6 octahedra, each octahedron sharing corners with six other octahedra. This structure is, however, not thermodynamically stable at ambient conditions but has been obtained and characterized at low temperatures or high pressures.³² In contrast, the ternary hydride Na_3AlH_6 decomposes (to NaH, Al, and H_2) at a temperature of 130 °C. It is reasonable to assume that the Na^+ ions in the decomposition

product NaH is about equally well stabilized as that in $\text{Na}_3\text{-AlH}_6$; hence, it appears safe to conclude that the AlH_6 coordination is more stable in an ionic solid as the isolated charged AlH_6^{3-} complex than in a covalent solid as corner-sharing neutral AlH_6 units. One may envision the crystal structure of $\alpha\text{-AlH}_3$ as an energy compromise between a desired valence of 3 and a desired coordination number of 6, the compromise being to adapt an arrangement in which all 6 corners of a given coordination polyhedron are shared with neighboring coordination polyhedra. Gallium is incapable of such a compromise because of the instability of the GaH_6 octahedral configuration. This is corroborated by the experimental findings for gaseous Ga_2H_6 which show gallium in tetrahedral coordination, and the hinted existence of liquid GaH_3 at -15 °C.³³

4. Conclusion

Whereas aluminum can adopt both tetrahedral and octahedral coordinations with hydrogen, gallium is restricted to tetrahedral coordination. From the point of view of hydrogen storage, the greater structural flexibility of Al could give rise to a number of metastable phase configurations with favorable mobility for hydride ions. In the quest for tailored hydrogen-storage materials, one may imagine stabilization of materials including AlH_4 structural units by the addition of a certain amount of Ga.

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Supporting Information Available: Crystallographic data files in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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