Does Al_4H_{14} – cluster anion exist ? High-level *ab initio* study.

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Rok wydania

2012

Czasopismo

Journal of Molecular Modeling

Numer woluminu

18

Strony

3427-3438

DOI

10.1007/s00894-012-1353-z

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

A comprehensive *ab initio* investigation using coupled cluster theory with the aug-cc-pVnZ, n = D,T basis sets is carried out to identify distinct structures of the $Al_4H_{14}^-$ cluster anion and to evaluate its fragmentation stability. Both thermodynamic and mechanistic aspects of the fragmentation reactions are studied. The observation of this so far the most hydrogenated aluminum tetramer was reported in the recent mass spectrometry study of Li et al. (2010) J Chem Phys 132:241103–241104. The four $Al_4H_{14}^-$ anion structures found are chain-like with the multiple-coordinate Al center and can be viewed approximately as comprising $Al_2H_7^-$ and Al_2H_7 moieties. Locating computationally some of the $Al_4H_{14}^-$ minima on the correlated *ab initio* potential energy surfaces required the triple-zeta quality basis set to describe adequately the Al multi-coordinate bonding. For the two most stable $Al_4H_{14}^-$ isomers, the mechanism of their low-barrier interconversion is described. The dissociation of $Al_4H_{14}^-$ into the $Al_2H_7^-$ and Al_2H_7 units is predicted to require 20-22 (10-13) kcal mol^{-1} in terms of ΔH (ΔG) estimated at T = 298.15 K and p = 1 atm. However, $Al_4H_{14}^-$ is found to be a metastable species in the gas phase: the H_2 loss from the radical moiety of its most favorable isomer is exothermic by 18 kcal mol^{-1} in terms of ΔH (298.15 K) and by 25 kcal mol^{-1} in terms of ΔG(298.15 K), with the enthalpic/free energy barrier involved being less than 1 kcal mol^{-1}. By contrast with alane $Al_4H_{14}^-$, only a weakly bound complex between $Ga_4H_{12}^-$ and H_2 has been identified for the gallium analogue using the relativistic effective core potential.

Słowa kluczowe

Al4H14— and Ga4H14— hydrogen-rich clusters, Coupled cluster calculations, Potential energy surfaces, Thermodynamic and kinetic stability