

Ligand coordination effects on gallium nanocluster reactivity

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Abstract

Stabilisation and modulation of nanocluster reactivity are key elements for the development of these materials as versatile and selective catalysts. This study presents a preliminary investigation of the interaction of ligands with a gallium nanocluster (Ga_{13}). The amphoteric nature of Ga_{13} means that both a Lewis base (NH_3) and a Lewis acid (BH_3) strongly adsorb to the surface of the cluster. More importantly, ligand coordination modifies the electronic structure of the cluster, leading to an enhancement of reactivity. In particular, NH_3 coordination was found to lower the energy barrier for H_2 chemisorption by 10% and BH_3 coordination led to reduction of the barrier by 20%. These results demonstrate the potential for ligand coordination as a means of accelerating reactions on cluster surfaces. Copyright © 2017 VBRI Press.

Keywords: Co-adsorption, cooperative effect, H_2 chemisorption, cluster stability.

Introduction

The adsorptive properties of nanocluster-based materials indicate potential for applications in gas separation, carbon capture and petrochemical operations, while their ability to activate small molecules provides opportunities for industrial catalysis and reduced emission energy technologies [1, 2]. Hampering these efforts, however, is the current inability to selectively and predictably control adsorption and reaction of small molecules on the surfaces of these species.

Transition-metal complexes have been utilised as catalysts for many decades and so it is not surprising that transition-metal clusters (TMCs) have been considered in the same light. Although there have been some successes [3, 4] the bonding in a metal cluster differs significantly from that of a metal complex [5, 6]. In particular, the evolution from covalent to metallic bonding, with increasing size, can be very rapid in metal clusters [7-9]. However, it is the coexistence of regions of localised and delocalised bonding on the surface of metallic clusters that facilitates adsorption and activation of small molecules [10-12].

Gallium is a unique metal in that it has a natural tendency to form covalently bonded Ga_2 subunits in both cluster and bulk structures (Fig. 1) [13, 14]. Therefore, even for large clusters there is a balance of covalent and metallic bonding, making these ideal materials to focus on for development of novel nanocatalysts. Inclusion of dopants into Ga clusters can lead to substantial changes in stability and corresponding modification of electronic properties [15-20]. Nevertheless, doping is predominantly a means of inducing broad changes in cluster reactivity.

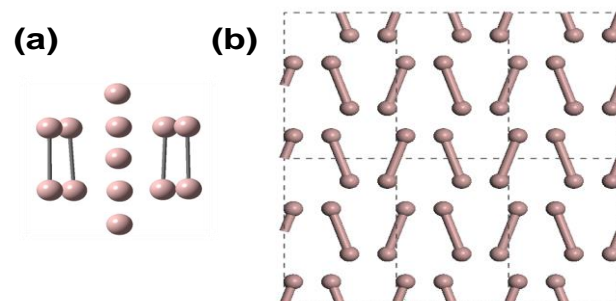


Fig. 1. Ga_2 subunits in (a) Ga_{13} and (b) bulk-Ga.

Ligands have been widely used in the synthesis of metal nanoclusters to control the kinetics of reduction/growth and to stabilize the growing particles [21, 22]. However, ligand coordination also offers the potential to subtly change the electronic structure of clusters, thereby providing a mechanism to modulate reactivity. For example, stereoselective additions require a fine control of active site geometry and kinetics. Electron donor or electron acceptor ligands may provide a means to enhance or diminish adsorption and reactivity of a target molecule at specific sites on a metal cluster surface and thereby facilitate fine control of the process.

The importance of ligand interactions to gallium nanochemistry has been highlighted by Schnöckel and co-workers [23-25] who have successfully produced gallium clusters on a laboratory scale using bulky protecting groups to stabilise the structures. The significance of these interactions is further demonstrated by the observed structural diversity. Different ligands lead to different

structural topologies, clearly indicating both steric and electronic influences impact on the arrangement of the metal atoms. However, the nature and size of these ligands generally inhibits the reactivity of the clusters. Therefore, investigation of a wider range of ligands is required to facilitate both stability and reactivity of these species.

Recent analysis suggests that gallium clusters are amphoteric and can interact with both Lewis acids and bases [26]. Adsorption of different ligands on the surface of gallium clusters will subtly alter the surface bonding and electronic structure of the cluster, which will impact on the reactivity. This study provides the results of a preliminary investigation of the effects of coordination of a selection of small molecules on a probe reaction, H₂ dissociative adsorption on Ga₁₃. The systems are then analysed in terms of structural, electronic and energy contributions.

Computational procedures

Standard hybrid density functional theory calculations were performed at the PBE0/6-311G(d,p) level using the GAUSSIAN09 computer program [27]. The interaction of ligands with the Ga₁₃ cluster was investigated by identifying isomers of Ga₁₃-L species, where L is BH₃ or NH₃. Vibrational frequency analysis was performed to confirm if the identified structures were true minima or saddle points on the potential energy surfaces. All energies reported in this study are in eV and include zero-point vibrational energy correction.

Ligand binding energies $E_b(L^1)$ are defined as:

$$E_b(L^1) = E(\text{Ga}_{13}L^1) - E(\text{Ga}_{13}) - E(L^1)$$

where, $E(\text{Ga}_{13}L^1)$ is the energy of the cluster with coordinated ligand, $E(\text{Ga}_{13})$ is the energy of the pristine cluster and $E(L^1)$ is the energy of the free ligand.

Activation energies were calculated as the difference in the energy of the transition state minus the energies of the reactants. Reaction enthalpies were obtained from the difference in energy of the products and reactants.

Results and discussion

The Ga₁₃ cluster has a 39-valence electron electronic configuration, with a distorted decahedral structure and is the smallest gallium cluster with near spherical geometry (Fig. 2a) [28-30]. The symmetry of Ga₁₃ means that it has distinct axial and equatorial regions and therefore differs from the widely studied isoelectronic Al₁₃ cluster, which has icosahedral symmetry. The lower symmetry of Ga₁₃ is also reflected in the shape and distribution of the frontier orbitals. The highest occupied molecular orbital (HOMO) is singly occupied (SOMO) and is located in the equatorial region of the cluster (Fig. 2b).

In comparison, the LUMO of this species is aligned along the axis of the cluster with prominent lobes on the axial surface atoms. The specific orientation of these

orbitals accounts for the regioselectivity observed for H-adsorption [20] and also points to some selectivity for the interaction with Lewis acids and bases.

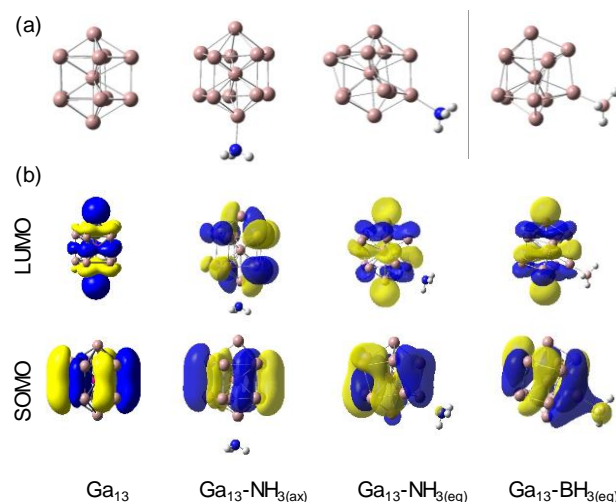


Fig. 2. (a) Structures and (b) Frontier Orbitals of Ga₁₃ and Ga₁₃-L clusters.

The DFT calculations reveal that ammonia (Lewis base) strongly adsorbs ($E_b(L^1) = -0.52$ eV) at the axial position of Ga₁₃ (Fig. 2a). This is consistent with a two-electron interaction between the highest occupied molecular orbital of ammonia (HOMO(NH₃)) and the lowest unoccupied molecular orbital of Ga₁₃ (LUMO(Ga₁₃)). In this case electron donation from ammonia leads to the formation of a dative covalent Ga-N bond with a bond length of 2.214 Å. Ammonia is also found to adsorb to the equatorial region of the cluster but with a lower binding energy ($E_b(L^1) = -0.47$ eV) and slightly longer bond length (2.236 Å). In this case the weaker interaction arises from a 3-electron interaction between HOMO(NH₃) and SOMO(Ga₁₃).

It is clear from Fig. 2 that adsorption in both locations leads to a distortion of the underlying cluster geometry. As expected the distortion arising from axial adsorption is localised to the axis of the cluster with the Ga-Ga bond furthest from the adsorption site showing the largest increase (0.192 Å). Similarly, equatorial adsorption leads to distortion of the central region of the cluster with the Ga-Ga bonds close to the adsorption site shortening (~0.05 Å) and the Ga-Ga bonds further away lengthening (~0.05 - 0.10 Å). The Lewis acid molecule BH₃ is only observed to interact with Ga₁₃ at an equatorial site on the surface of the cluster ($E_b(L^1) = 0.52$ eV). This is consistent with a one electron frontier orbital interaction, in this case between the LUMO(BH₃) and SOMO(Ga₁₃). The Ga-B bond length in Ga₁₃-BH₃ is calculated to be 2.165 Å. Again, this interaction disrupts the structure of the cluster with an increase in the length (~0.1 Å) of the Ga₂ subunit at the adsorption site and also one of the axial Ga-Ga bonds (~0.1 Å).

The effects of these ligand interactions on the frontier orbitals of the Ga₁₃ cluster are depicted in Fig. 2b. Axial adsorption of NH₃ has essentially no effect on the size or

location of the HOMO of Ga₁₃. However, the two-electron interaction between the ligand and the cluster lowers the energy of the LUMO into the bonding region, thereby making the original LUMO+1(Ga₁₃) the new LUMO for the aggregate structure. This orbital has much more anti-bonding character than LUMO(Ga₁₃), which will impact on further interactions with electron donors.

Equatorial adsorption of both NH₃ and BH₃ disrupts the SOMO of Ga₁₃ but it retains a similar nodal structure within the cluster. The LUMOs of the Ga₁₃-NH₃(eq) and Ga₁₃-BH₃(eq) structures are essentially the same as the LUMO of Ga₁₃.

The above results indicate that equatorial adsorption stabilises the cluster without significantly altering the distribution of the frontier orbitals. Dissociative adsorption of H₂ onto the clusters was used as a probe reaction, to directly test the impact of these ligands on reactivity. In keeping with the pattern of adsorption of the ligands, two sites were specifically investigated for H₂ dissociation, an axial bridge site (b1) and an equatorial bridge site (b2) (Fig. 3).

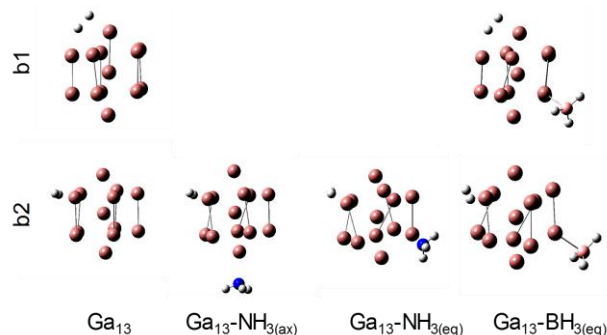


Fig. 3. Transition structures for H₂ dissociative adsorption on Ga₁₃ and Ga₁₃-L clusters.

Transition states were located for both sites on the clean Ga₁₃ cluster and the BH₃ coordinated cluster (Ga₁₃-BH₃). However, for the ammonia-coordinated systems it was only possible to locate TSs for the equatorial bridge site. In fact, attempts to locate the b1 TS for the Ga₁₃-NH₃(ax) system resulted in transformation to the corresponding b2 transition structure. Table 1 presents key geometric parameters from these transition structures including the distances between each H atom and the nearest gallium atoms (Ga...H¹ and Ga...H²) and the H-H distance for the dissociating H₂ molecule (H¹...H²).

The data for the Ga₁₃ and Ga₁₃-BH₃(eq) systems reveal that there are site specific differences in the transition structure parameters. In general, the H atoms are closer to one or more gallium atoms in the b2 TSs than in the b1 TSs indicating greater development of the Ga-H bonds. Furthermore, the H¹...H² distances in the b2 TSs are significantly longer reflecting a higher degree of dissociation in the H₂ molecule.

The two Ga₁₃-NH₃ systems have remarkably similar transition structure parameters despite the difference in location for ligand coordination. In addition to this, the Ga...H¹ and H¹...H² distances of the ammonia systems are

quite similar to the corresponding values for the b2 Ga₁₃-BH₃(eq) system. However, the Lewis base ligand (NH₃) appears to also promote development of the second Ga-H bond in the TS to a greater extent than the Lewis base ligand (BH₃). A key observation from these values is that chemisorption of H₂ at the b2 appears to proceed through a later or more product like transition state.

Table 1. Selected geometric parameters (Å) for transition structures for H₂ adsorption on Ga₁₃ and Ga₁₃L (L = NH₃ or BH₃) clusters.

Cluster	Site	Ga...H ¹	Ga...H ²	H ¹ ...H ²
Ga ₁₃	b1	1.721	1.872	1.098
Ga ₁₃	b2	1.700	1.702	1.311
Ga ₁₃ -NH ₃ (ax)	b2	1.692	1.726	1.247
Ga ₁₃ -NH ₃ (eq)	b2	1.693	1.738	1.198
Ga ₁₃ -BH ₃ (eq)	b1	1.735	1.896	1.028
Ga ₁₃ -BH ₃ (eq)	b2	1.681	1.896	1.252

The energy barriers for the identified transition states are presented in Table 2.

Table 2. Energetic data for H₂ adsorption on Ga₁₃ and Ga₁₃L (L = NH₃ or BH₃) clusters.

Cluster	H ₂ Site	ΔE [‡]	ΔH
Ga ₁₃	b1	1.283	0.078
Ga ₁₃	b2	1.036	0.257
Ga ₁₃ -NH ₃ (ax)	b2	0.936	0.249
Ga ₁₃ -NH ₃ (eq)	b2	0.938	0.085
Ga ₁₃ -BH ₃ (eq)	b1	1.320	-0.105
Ga ₁₃ -BH ₃ (eq)	b2	0.822	0.159

H₂ dissociation at the axial site (b1) of Ga₁₃ has a higher barrier (+0.247 eV) than for the equatorial site. Therefore, H₂ chemisorption should preferentially occur at the b2 site. Although both pathways are predicted to be endothermic, the ΔH for the b1 pathway indicates that overall it is almost energy neutral. The greater endothermicity of the b2 pathway is consistent with a later transition state identified from the geometric parameters and in line with the Hammett postulate of reaction mechanisms. The underlying geometry of the Ga₁₃ cluster shows relatively little distortion in the transition structure of either pathway that suggests that the differences in ΔH[‡] are due primarily to electronic contributions. H-H dissociation requires injection of electrons into the H₂ anti-bonding orbital (σ*). The SOMO of Ga₁₃ has an appropriate nodal structure to facilitate overlap with σ*(H₂) in the b2 position but not the b1 position. Reaction at the b1 site therefore requires interaction with a deeper occupied orbital of the cluster, which contributes to the higher energy barrier for H₂ adsorption in the axial region.

Coordination of the NH₃ or BH₃ ligands is found to have a significant effect on the activation energy for H₂ dissociative adsorption on the cluster. Reaction at the b1 site remains unfavourable in the Ga₁₃-BH₃(eq) and in fact the calculations predict a higher ΔH[‡] relative to Ga₁₃. However, for all three Ga₁₃L structures there is a

reduction in ΔH^\ddagger for H_2 adsorption at the b2 site. For the ammonia-coordinated systems this corresponds to a decrease in ΔH^\ddagger of approximately 10% (~ 0.10 eV). However, for the $Ga_{13}\text{-BH}_3(\text{eq})$ system the reduction is $\sim 20\%$ (0.21 eV) compared to Ga_{13} , which would correspond to a substantial increase in reaction rate. In the simple system considered in this study an electron acceptor ligand (Lewis acid) leads to the largest increase in reactivity. Earlier studies have shown that changes in the strength of surface bonds of Group 13 clusters can have a significant effect on cluster reactivity [12, 26] Although these changes in bonding and reactivity have previously been implemented through doping, the identification of similar results from ligand coordination provides an additional technique for modulating the reactivity of these species.

Conclusion

DFT calculations reveal that simple Lewis base and Lewis acid molecules will strongly coordinate ($E_b(L^1) = \sim 0.5$ eV) to the surface of a gallium nanocluster. The stabilization of the cluster by ligand coordination was also found to subtly alter the orbitals of the cluster in such a way as to modulate the reactivity of the species. Using H_2 chemisorption as a probe reaction, ammonia coordination was found to lower the reaction barrier by 10% while Lewis acid coordination (BH_3) lowered the barrier by as much as 20%, compared to the pristine cluster. A degree of regioselectivity was observed for reaction on the cluster surface with the equatorial region of the cluster more favoured than the axial region. The combination of cluster stabilization and enhanced reactivity achieved by ligand coordination identifies this as an important area for further research with the potential to develop novel nanocatalysts.

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Author's contributions

Conceived the plan: David Henry; Performed the experiments: David Henry; Wrote the paper: David Henry. Author has no competing financial interests.

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