

Theoretical study of aromaticity in inorganic tetramer clusters

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Abstract. Ground state geometry and electronic structure of M_4^{2-} cluster ($M = B, Al, Ga$) have been investigated to evaluate their aromatic properties. The calculations are performed by employing the Density Functional Theory (DFT) method. It is found that all these three clusters adopt square planar configuration. Results reveal that square planar M_4^{2-} dianion exhibits characteristics of multifold aromaticity with two delocalised π -electrons. In spite of the unstable nature of these dianionic clusters in the gas phase, their interaction with the sodium atoms forms very stable dipyramidal M_4Na_2 complexes while maintaining their square planar structure and aromaticity.

Keywords. Inorganic tetramer clusters; aromaticity; density functional theory.

1. Introduction

The concept of aromaticity is used for understanding the enhanced stability of benzene and its derivatives. Recently, the applicability of the aromaticity concept has been extended to metallic clusters in combined photoelectron spectroscopy and *ab initio* molecular orbital calculational investigation of M_4^{2-} cluster (Al, Ga and In) clusters.¹ The Al_4^{2-} unit has square planar shape with two delocalised π electrons in the highest occupied molecular orbital (HOMO). The $4n + 2$ electron counting rule is satisfied with the two delocalized π electrons, but the two σ bonded MOs below the HOMO also contribute to the stability, providing multifold aromaticity (π and σ) for the system. These concepts were then extended to other isoelectronic systems B_4^{2-} , Ga_4^{2-} . In recent times many articles has been published^{2–33} to corroborate the aromatic and anti-aromatic character of small metal and main group element clusters. Most of these studies published in recent years have concentrated on charged clusters. However, very few studies on neutral clusters are reported. In our previous work³⁴ we have reported some stable neutral clusters (Al_2Si_2 , Al_2Ge_2 , Ga_2Si_2 , Ga_2Ge_2 , Si_3Be , Si_3Mg , Ge_3Be , Ge_3Mg , Al_3P , Al_3As , Ga_3P , and Ga_3As) with 14 electrons in the valance shell and established their aromatic behaviour. The aromatic character of these clusters has been analysed based on planarity, electronic stability (hardness, large ionization potential and low electron affinity), nu-

clear independent chemical shift (NICS) values and their molecular orbital pictures. Further, it was found that after interacting with hydrogen atoms the structural integrity and the planarity of these clusters is retained.

Mercero *et al*⁶ using sandwich like complexes of Al_4^{2-} , pointed out that doubly charged species like Al_4^{2-} , B_4^{2-} , Ga_4^{2-} are expected to be rather unstable in the gas phase due to large intramolecular coulomb repulsion. The instability of dianions was also predicted by Kuznetsov *et al*⁹ and Boldyrev *et al*²⁹. In the present work, we have studied dianion systems, and their corresponding neutral cluster, Al_4Na_2 , B_4Na_2 , Ga_4Na_2 , in which the double charge of the system has been neutralized by the sodium atoms. The objective of the present study is to know what is the change in the geometry, structural integrity, and aromaticity of the dianion cluster after interaction with two sodium atoms. We use the conventional criteria of aromaticity such as chemical (extra stability), and magnetic criteria (i.e. nuclear independent chemical shift (NICS)) to confirm the aromatic character of these clusters.

2. Computational details

Ab-initio molecular orbital theory based on LCAO approach has been employed to elucidate the ground state geometries of these clusters. For this purpose, initial geometry optimisation was done using the hybrid exchange correlation energy functional commonly known as B3-LYP.³⁶ The notation B3 implies three

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parameter Becke exchange functional³⁶ and LYP indicates correlation functional as described by Lee-Yang-Parr.³⁶ A standard split-valence with polarization functions (6-311G + (d)) was employed as basis set for all these calculations [6-31 + G(d) in case of the cluster with Ga atom]. All the calculations were carried out using the GAMESS software.³⁷ The nuclear independent chemical shift (NICS) values were calculated using the gauge-including atomic orbitals (GIAO) method at the B3LYP level of theory using Gaussian-98 software.³⁸

3. Results and discussion

For B_4^{2-} , Al_4^{2-} and Ga_4^{2-} clusters, the lowest energy structure was square planar with D_{4h} symmetry. Three dimensional tetrahedron and other geometries resulted in significantly higher energy as compared to the planar configurations. In table 1 we have summarized the results of the geometrical parameters, total energies, binding energies (BE), highest occupied molecular orbital (HOMO) energy, lowest unoccupied molecular orbital (LUMO) energy and the gap between HOMO and LUMO levels.

From this table it is clear that the energy eigenvalues for the HOMO are positive for negatively charged clusters B_4^{2-} , Al_4^{2-} and Ga_4^{2-} . A positive value represents an unbound state or in other words reflects that doubly negatively charged clusters are extremely reactive. In earlier work³⁴ we have shown that similar isoelectronic neutral clusters like Al_2Si_2 , Ga_2Si_2 have negative energy eigenvalues of the highest occupied

molecular orbitals (HOMO), and also the gaps between LUMO and HOMO levels vary between 2.5 and 3.5 eV indicating that these neutral cluster are much more stable than double charged negative ions. Hence it is desirable to find out stable neutral clusters or in other word, the clusters in which the charge on these anionic cluster has been neutralized by some metal atoms. For this purpose we have carried out the geometric and electronic structure optimisation for a series of tetramer binary clusters Al_4Na_2 , B_4Na_2 , Ga_4Na_2 . The choice of these neutral clusters is based on their iso-electronic configuration with the doubly charged aromatic clusters discussed above.

In table 2 we have summarized the results of the total energies, geometrical parameters (M–M and M–Na (Å)) binding energies (BE), Highest occupied molecular orbital (HOMO) energy, lowest unoccupied molecular orbital (LUMO) energy and the gap between HOMO and LUMO levels for Al_4Na_2 , B_4Na_2 , Ga_4Na_2 cluster. From the results it is clear that even after interacting with two sodium atoms the structural integrity and the planarity of these dianionic clusters is retained.

To confirm the stability of the M_4Na_2 species we have calculated the energies for the hypothetical reaction $M_4Na_2 \rightarrow M_4^{2-} + 2Na^+$. The energies are as follows

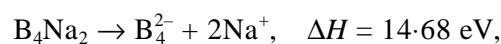


Table 1. Total energies, interatomic separations (Å), binding energy per atom (BE), energy eigenvalues of the highest occupied molecular orbitals (HOMO), energy eigenvalues of the lowest unoccupied molecular orbitals (LUMO) and gap between HOMO and LUMO levels.

Cluster	Total energy (a.u.)	M–M	BE (eV)	HOMO (eV)	LUMO (eV)	Gap (eV)
B_4^{2-}	–99.010998	1.63	2.75	4.74	6.15	1.41
Al_4^{2-}	–969.5387656	2.59	1.12	2.98	4.91	1.94
Ga_4^{2-}	–7691.7510659	2.50	1.54	3.02	4.71	1.69

Table 2. Total energies, interatomic separations (M–M and M–Na (Å)), binding energy per atom (BE), energy eigenvalues of the highest occupied molecular orbitals (HOMO), energy eigenvalues of the lowest unoccupied molecular orbitals (LUMO) and gap between HOMO and LUMO levels.

Cluster	Total energy (a.u.)	M–M	M–Na	BE (eV)	HOMO (eV)	LUMO (eV)	Gap (eV)
B_4Na_2	–423.647475	1.66	2.67	2.61	–3.19	–1.48	1.71
Al_4Na_2	–1294.129737	2.62	3.16	1.31	–3.85	–2.01	1.84
Ga_4Na_2	–8016.361335	2.52	3.12	1.74	–3.83	–1.94	1.89

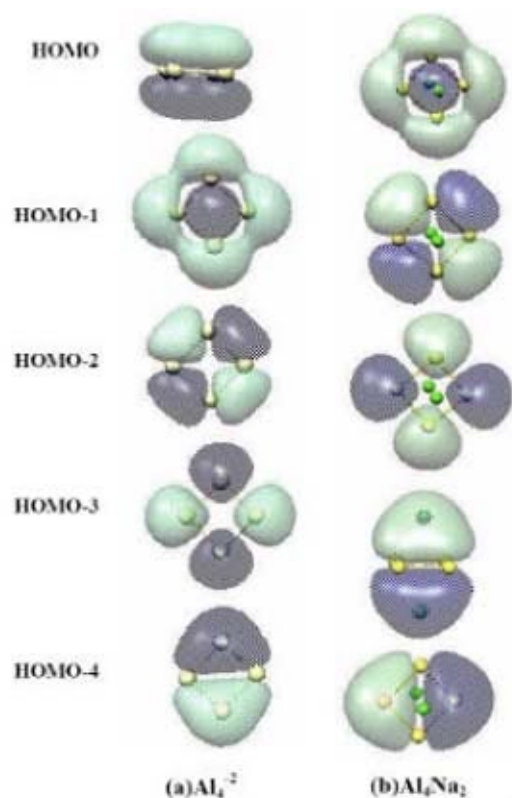


Figure 1. Spatial orientation of the top five occupied molecular orbitals for Al_4^{2-} and Al_4Na_2 cluster.

Table 3. NICS values of the clusters.

Cluster	NICS (0.0)	NICS (1.25)
B_4^{2-}	-29.53	-3.04
B_4Na_2	-25.51	-19.13
Al_4^{2-}	-34.36	-23.15
Al_4Na_2	-12.58	-23.03
Ga_4^{2-}	-32.16	-20.21
Ga_4Na_2	-14.04	-24.59

All reactions are highly endothermic, indicating that the M_4Na_2 species are stable towards decomposition. In order to understand the nature of bonding, the spatial orientations of five occupied molecular orbitals (HOMO to HOMO-4) have been worked out for all these clusters studied and representative results are shown in figure 1. It is clear from this figure that all the clusters have at least one of the HOMO energy levels representing π type molecular orbitals where two electrons are delocalised over all four atoms. In addition to retaining their structural integrity, these dianionic clusters after their interaction with sodium atoms and hydrogen, maintain the spatial orientation

of the HOMO energy levels also except for the fact that their ordering is changed.

Aromaticity of all these clusters has also been studied by using the nucleus independent chemical shift (NICS), a method developed by Schleyer and co-workers,³⁵ which is a magnetic criterion that mirrors the ring current. In this method, the nuclear magnetic resonance (NMR) parameters are calculated for a ghost atom, usually placed at the centre of the ring, and the NICS value is the negative of the isotropic magnetic shielding constant at the ghost atom. Systems with negative NICS values are aromatic, since negative values arise when diatropic ring current (shielding) dominates, whereas systems with positive values are antiaromatic because positive values arise when paratropic current (deshielding) dominates. The NICS (0.0) values calculated at the centre of the ring is influenced by σ -bonds, whereas the NICS (1.25) values calculated 1.25 Å out of the plane are more affected by the π -system. The results obtained are given in table 3. From the table it is clear that the M_4^{2-} ring in the M_4Na_2 species exhibits characteristics of aromaticity or in other words it retains its aromaticity.

4. Conclusion

In summary, the equilibrium geometries and electronic structures of M_4^{2-} and M_4Na_2 clusters ($\text{M} = \text{B}, \text{Al}, \text{Ga}$) have been studied by hybrid density functional theory (B3LYP) formalism. The results show that M_4^{2-} clusters favour square planar structure as a global minimum. In spite of their natural instability in terms of chemical reactivity, these dianionic clusters co-ordinate to sodium atoms to form very stable dipyrmidal structures, M_4Na_2 , without losing their planarity and aromaticity.

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