Density Functional Study of Ga_8 and Ga_{13} Clusters

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Introduction

Amongst others terphenyl-based ligands find widespread use in the preparation of metalloid cluster compounds and other structurally interesting substances [1,2]. Using the well-known ligand system L {2,6-$Mes_2(C_6H_3)$, Mes=2,4,6-trimethylphenyl} Ga_8 and Ga_{13} clusters could be synthesized and characterized by various spectroscopic methods. To gain information on the bonding properties and sterical characteristics DFT calculations on the PW91/TZ2P level as implemented in ADF were performed.

Input Geometries

Only few group 13 element clusters are known in literature, most of which are charged [3]. We synthesized Ga_8 and Ga_{13} clusters and used the X-ray crystal structure data as input in order to analyze bonding and sterical properties and to study the orbitals. Variation of the substituents was performed to study the steric effects of the terphenyl groups. A deformation of the inner core structure was observed.

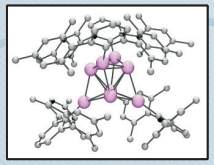


Fig. 1 Crystal structure of Ga_8L_4.

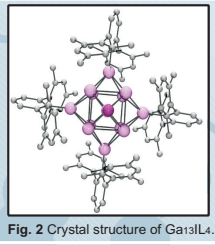


Fig. 2 Crystal structure of $Ga_{13}IL_4$.

Ga	
I	

	Ga_8	Ga_{13}
Ga-C [Å]	2.009-2.017	1.989
Ga-Ga [Å]	2.408-2.923	2.568-3.035
Ga-I [Å]	---	2.551

Model Substances

In case of Ga_{13} replacing the ligand systems by methyl groups or simulating only the Ga core of the molecule led to a maintenance of the cubic inner core of 8 Ga atoms. The variation of the substituents of Ga_8, in contrast, led to a deformation of the inner tetrahedron.

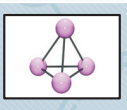


Fig. 3 Geometry of the inner core of optimized Ga_8L_4.

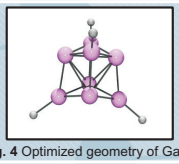


Fig. 4 Optimized geometry of Ga_8Me_4.

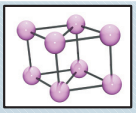


Fig. 5 Optimized geometry of non-substitued Ga_8.

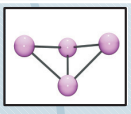


Fig. 6 Geometry of the plain optimized inner core.

Orbital Visualization

Visualization of the frontier orbitals shows interesting aspects of stability and steric properties. The HOMO of Ga_8Me_4, e.g., is centered in the middle of the cluster. NICS calculations will yield information on aromaticity in the Ga_8 center. The HOMO of $Ga_{13}IMe_4$, in contrast, is situated at the backbone of the inner tetrahedral core, offering a potential reactive site in the nevertheless thermodynamically stable system. The steric demand of L leads to an enhanced kinetic stabilization of $Ga_{13}IL_4$.

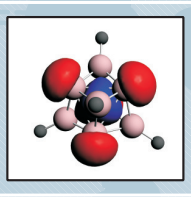
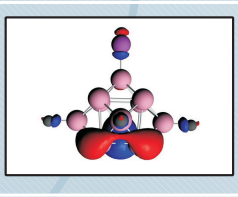


Fig. 7 HOMO of Ga_8Me_4.

Fig. 8 HOMO of $Ga_{13}IMe_4$.



Conclusion & Outlook

Ga_8 and Ga_{13} clusters were characterized on the PW91/TZ2P level. Interesting geometry changes were observed when replacing the terphenyl ligand systems. Future investigations will yield information on bonding properties and aromaticity in the inner cores of the clusters. In addition, a comparison between charged and uncharged analogs will be performed.

Notes & References

[1] E. Rivard, P.P. Power, Inorg. Chem., 46, 10047 (2007).
[2] A. F. Richards, B. E. Eichler, M. Brynda, M. M. Olmstead, P. P. Power, Angew. Chem. Int. Ed., 44, 2546 (2005).
[3] M. Driess, Molecular Clusters of the Main Group Elements (2004).