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Theoretical Studies on the Penta-Atomic Planar Coordinate Carbon Molecules [CGa_3Sn] and [CGa_3Sn]$^-$ [1]

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Abstract—The pentaatomic [CGa_3Sn] and [CGa_3Sn]$^-$ species were studied via density functional theory (DFT). Six planar geometry isomeric structures were gained, and one of them exists tetracoordinate planar carbon atom, respectively. To gain a better understanding about which electronic factors contribute to the stabilization of tetracoordinate planar carbon structures, natural bond orbital (NBO) analysis and the nucleus independent chemical shifts (NICS) were calculated. This analysis suggests that the presence of 18 valence electrons is crucial for planar geometries to be stable and preferred over tetrahedral structures.

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INTRODUCTION

Since Hoffmann and co-workers proposed the idea of planar tetracoordinate carbon (ptC) molecules at 40 years ago [1], violating the most important paradigm of tetrahedral carbon atom, there have been substantial research efforts to design new molecules that may contain tetracoordinate carbon by theoreticians and experimentalists. In an earlier work, Schleyer and Boldyrev computationally and experimentally predicted that CSi_2X_2 (X = Al, Ga) and CGe_2Al_2 were locally stable structures containing a planar tetracoordinated central carbon [2, 3], and they also codified design rules for achieving planar hypercoordinate structures. There should be a good “fit,” both geometric (the ring size and the covalent radius of the central atom should match) and electronic (degenerate molecular orbitals should be equally occupied and a Hückel π-electron count is helpful, but not always mandatory). It also was recognized that the σ as well as the π system contributed to the planar stabilization. Stimulated by these theoretical findings, a series of planar tetracoordinate carbon species, such as CAl_4^- [4] and CAl_4^{2-} [5] with D_{4h} symmetry, [Al_3XC] and [Al_3XC]$^-$ (X = Si, Ge) [6] with C_{2v} symmetry and their relatives were identified in gas-phase photoelectron spectroscopy (PES) experiments. In 2010, Ding [7] computationally predicted that [Cal_3X] and [Cal_3X]$^-$ (X = Sn, Pb) were globally stable structures containing a planar tetracoordinated central carbon. It is expected that such hetero-doped ptC species are important to materials science. Compared with tetracoordinate planar carbon species, hypercoordinate planar carbon species be more fascinating to theoreticians and experimentalists. In particular, computational chemistry has made dramatic advances, enabling the prediction of higher coordination in planar carbon species. CAl_5^+ [8], C_5^{2-} [9–11], CBe_5 and CBe_5^{4-} [12] species with D_{5h} symmetry have a pentacoordinate carbon. CB_6^{2-} and CB_7^- species contain hexa-coordinate and hepta-coordinate planar carbon species with high symmetries of D_{6h} and D_{7h}, respectively [13–15]. The CB_8 clusters have been theoretically proposed to be octacoordinated planar carbon species [16]. The theoretically has been predicted stabilization of hypercoordinate group 14 elements Si, Ge, and Sn in the center of boron rings [17–19].

In this article, we will first report a quantum chemical study of the molecules [CGa_3Sn] and [CGa_3Sn]$^-$. The pentaatomic molecules were selected with several reasons. For one thing, only interactions between the central carbon and the ligands and the ligand-ligand interactions can be responsible for the planar arrangement in such species. Furthermore, planarity in the species is not enforced by their molecular architecture, but rather by their intrinsic and unique electronic structure. For another, we are going to want to explore how varying the size of the ligand atoms affects stability of the structures.

COMPUTATIONAL METHODS

We were carried out for geometry optimization and vibrational frequency analysis by hybrid DFT method, which includes a mixture of Hartree-Fock exchange with density functional exchange correlation (B3LYP) [20–22]. The SDD basis set for Sn standard 6–311+G(d)

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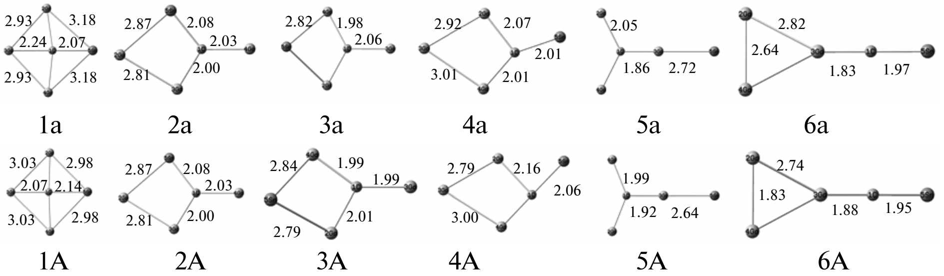

Fig. 1. Parameters (structure, labels, Full point group and State) for the [CGa_3Sn] and [CGa_3Sn]$^-$ species obtained at the B3LYP method. The relative energies (kJ/mol) are computed at the CCSD(T)/SDD/6-311+G(2df) level theory using the coordinates optimized from the B3LYP/SDD/6-311+G(d) level theory.

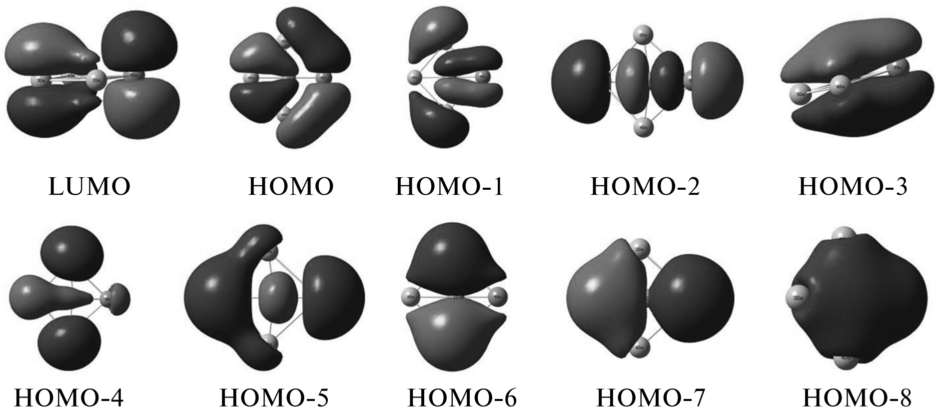

Fig. 2. The molecular orbitals pictures of [CGa_3Sn] for structure 1.

polarized split-valence basis set for other atoms were used. Vibrational frequency analyses confirmed that each structure is at a minimum without imaginary frequency. Using these geometries, single point energies were evaluated at the CCSD(T)/SDD/6-311+G(2df) level. The atomic charges were computed within the Natural Population Analysis (NPA). Wiberg indexes were evaluated and used as bond strength indicators. Natural bonding orbital (NBO) analysis was performed with NBO Version 3.1 [23, 24] incorporated in the Gaussian 09 program. Nucleus-independent chemical shifts (NICS, in ppm) [25, 26] were computed using the gauge-independent atomic orbital (GIAO) method [27, 28] at B3LYP/SDD/6-311+G(d) level. All the calculations were performed with the Gaussian-09 program [29].

RESULTS AND DISCUSSION

Structures and energy. Geometric parameters for the [CGa_3Sn] and [CGa_3Sn]$^-$ species computed at the B3LYP/SDD/6-311+G(d) level are illustrated in Fig. 1. High spin states were also examined for each of these low spin structures but were found to be substantially higher in energy and thus were not considered further. Relative energies included zero-point energy contributions without scaling obtained at the two levels of theory. Six kinds of planar geometry isomeric structures were gained for both species. Structure 1 hold central planar tetracoordinate carbons, while structures 2–5 possess central tricoordinate carbons, and structure 6 is two-fold coordination. From relative energies, structure 1 is always the lowest energy, which indicates that structure 1 is indeed the global minimum on the potential energy surface. The relative energies between structure 1 and the second lowest-energy isomers are more than 93.99 kJ/mol (93.99 kJ/mol for CGa_3Sn, 123.92 kJ/mol for [CGa_3Sn]$^-$, respectively). Meanwhile classic the tetrahedral structure for tetracoordinated carbon had been optimized as input geometry and converged to structure 1, further confirming that the structure 1 was true minimum on its potential energy surface.

Molecular orbital analysis. To understand the planarity and structural integrity of the species under the investigation, we analyzed their valence molecular orbitals shown in Fig. 2. The molecular orbits of neutral molecular produced analogous figure as those of anions. We can take [CGa_3Sn] as an example. For [CGa_3Sn], there are a totally delocalized π orbital (HOMO-3) with the dominating contribution from the $2p_z$ orbital of the central carbon atom and the p_z orbital of the Ga and Sn atoms, and an extensively

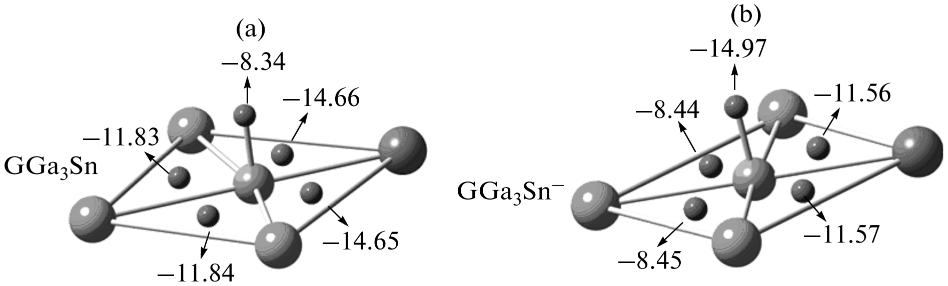

Fig. 3. Computed NICS (ppm) of the structures for $[CGa_3Sn]$ (a) and $[CGa_3Sn]^-$ (b).

delocalized peripheral σ orbital (HOMO-5), which favor the planar structure. Furthermore, the large HOMO–LUMO gap (2.44 V for $[CGa_3Sn]$, 2.21 V for $[CGa_3Sn]^-$, respectively) also suggests high stability of the tetracoordinate planar carbon in the four molecules.

Natural bond orbital analysis. NBO analysis indicates charge transfer from the peripheral Ga and Sn ligands to the central electronegative C atom. The central carbon atom carries considerable negative charges of above −2.36 e, while other atoms hold positive charges. Taking $[CGa_3Sn]$ (or $[CGa_3Sn]^-$) as an example, it can be seen that the natural atomic charges on the peripheral Ga(2), Ga(3), Ga(4), Sn(5) and central C(1) atoms are +0.56, +0.53, +0.56, +0.82 (or +0.56, +0.53, +0.56, +0.82) and −2.47 e (or −2.36), respectively. Note that the carbon acts as a σ acceptor, and this compensates for the donation of the carbon $2p_z$ electrons to the π bonding, which can be proved by the valence population of the tetracoordinate planar carbon ($2s^{1.70}2p_x^{1.62}2p_y^{1.61}2p_z^{1.54}$ for $[CGa_3Sn]$, $2s^{1.66}2p_x^{1.65}2p_y^{1.58}2p_z^{1.46}$ for $[CGA_3Sn]^-$, respectively). The relatively high $2p_x$ and $2p_y$ occupancies and lower occupancies in $2p_z$ orbitals are manifestations of the back-donation. Interestingly, negative charges in central carbon atom and positive charges peripheral Ga, Sn will reduce from neutral molecule to their monovalence anion, and the biggest change of charges are 0.30 for Sn, which implies that all the additional one electrons fill in the valence orbitals of the peripheral Ga, Sn atoms.

Wiberg bond indexes (WBIs) were evaluated and used as bond strength indicators. Some wiberg indexes for structure 1 are given below:

Structure 1	C(1)–Sn(5)	C(1)–Ga(2)	C(1)–Ga(3)	C(1)–Ga(4)	Ga(2)–Ga(3)	Ga(2)–Sn(5)
$[CGa_3Sn]$	1.14	0.43	0.38	0.43	0.26	0.19
$[CGa_3Sn]^-$	1.04	0.52	0.53	0.52	0.24	0.49

Note that the WBIs for C(1)–Sn(5) is the biggest (>1.04). WBIs for C(1)–Sn(5) would reduce from neutral molecule to their monovalence anion, consistent with the reduction of charge and increase of C(1)–Sn(5) bond length, while the other WBIs will increase. And the total WBIs of the C atom in neutral molecule strengthen compared to their monovalence anion. However, the charges for central carbon and peripheral Ga rueduce, while WBIs between central carbon and Ga increase, which can be explained that ionic character of the C–Ga rueduces, and covalent character of them increase.

Aromaticity. NICS can help predict and understand some unique properties of a molecule, especially, its stability due to aromatic stabilization, which is based on the negative of the magnetic shielding computed at or above the geometrical centers of rings or clusters. Systems with negative NICS value is aromatic. To gain a better understanding of the aromaticity of these species, the NICS(0) in the middle of $[CGa_3Sn]$, $[CGa_3Sn]^-$, triangles and NICS(1) were evaluated at the ghost atom located above the C atom by 1.0 Å. As shown in Fig. 3, NICS(0) and NICS(1) are negative value (<–8.34 ppm), which implies that they are both σ and π aromaticity. This situation denotes significant σ and π electrons delocalization that we can be concretely proved by the pictures of molecular orbitals shown in Fig. 2.

In summary, $[CGa_3Sn]$ $[CGa_3Sn]^-$, possessing 17 and 18 valence electrons, we were optimized at the B3LYP/SDD/6-311+G(d) level theory. Six planar geometry isomeric structures were gained for both species. Structure 1 which was analyzed in detail hold tetracoordinated central carbon and global minimum on its potential energy surface. The bonding between the central C and peripheral atoms may be interpreted from the donation interaction coming from the peripheral atoms to the central C, and from the back-donation from the latter to the former. The NICS value denotes σ and π aromaticity for structure 1, which is one of the fundamental reasons to understand the stability of the structure, this analysis suggests that the presence of 18 valence electrons is crucial for planar geometries to be stable and preferred over tetrahedral structures. It is our belief that understanding the bonding in such molecules is important for future progress in the design molecules and compounds with tetracoordinated planar carbon.

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