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IOAN SILAGHI-DUMITRESCU[a] and BRUCE KING[b]

ABSTRACT. Hybrid DFT B3LYP geometry optimizations on Ge_n^z (n=5 – 14), z= -6, -4, -2, 0, +2, +4,+6) have been undertaken in order to understand the structure of some post-transition metal cluster anions established experimentally by X-ray crystallography. Distortions from the expected geometries are interpreted in terms of hypo- or hyperelectronic counting of the skeletal electrons. Deviations from the Wade-Mingos rules noticed in several cases can be related to the use of the "external" electron pairs in the skeletal bonding.

Keywords: *germanium clusters, hypoelectronic clusters, hyperelectronic clusters, B3LYP DFT calculations.*

INTRODUCTION

Zintl phases discovered in 1930 [1-4] as the result of reaction of post-transition metals with sodium in liquid ammonia proved to be the beginning of an extremely fertile field of chemistry. Among other applications, such systems are considered as precursors for various nanomaterials. Zintl phases exhibit structural patterns (Table 1) varying from elemental structure shapes (a) to isolated tetrahedral units (b), oligomeric tetrahedral units (c), polymeric tetrahedral units (d), and highly condensed tetrahedral units (e). In all of these systems the covalently bound atoms share pairs of electrons in localized 2 center - 2 electron bonds. Unlike these species, a wealth of other types of structures (f) have been discovered where the number of skeletal electrons is different from that required by two centre bonds.

For the latter type of M_n systems the Wade-Mingos rules [18-21] state that if the number of skeletal electrons is 2n+2, the most spherical, closed deltahedral structure is expected. If however the number of skeletal electrons exceeds 2n+2 (hyperlectronic systems) the most favoured structures have non triangular faces (one for the so called *nido* clusters; two or one large open face for the so called "arachno" clusters). If the number of skeletal electrons is less then 2n+2 (hypoelectronic systems) several possibilities can occur to overcome this deficiency. Thus, the same polyhedron as in the case of 2n+2 electrons might be observed (but with some localized skeletal electrons), or a smaller

[a] *Universitatea Babes-Bolyai, Facultatea de Chimie si Inginerie Chimică, Str. Kogalniceanu, Nr. 1, RO-400084 Cluj-Napoca,Romania, isi@chem.ubbcluj.ro*
[b] *Department of Chemistry, University of Georgia, Athens, Georgia, rbking@chem.uga.edu*

polyhedron with some of the triangular faces capped by one atom, or ‘flattening” of the 4-vertex atoms in such a way that the otherwise external electron pairs are drawn into the skeletal bonding.

Table 1.

Structural patterns encountered in Zintl phases.

	Phases	Reference
a	P_4 like Si_4^{4-}	5
	Si_4^{6-}	5
	Black phosphorus type $_\infty^2[As_3^{2-}]$, $_\infty^2[Sb_3^{2-}]$,	6,7
b	Isolated tetrahedral units: SiP_4^{8-}, $SiAs_4^{8-}$ GeP_4^{8-},$SnAs_4^{8-}$	8,9
c	Oligomeric tetrahedral units: $Si_2P_6^{10-}$, $Ge_2P_6^{10-}$, $Sn_2P_6^{10-}$	10-12
d	Polymeric tetrahedral units: $_\infty^1[SnP_3^{5-}]$, $_\infty^1[E(14)E(15)_2]^{2+}$ E(14)=Si,Ge,Sn, E(15)=P,As	13-14
e	Highly condensed tetrahedral frameworks: $^3_\infty[GaX_2^{3-}]$ X = P, As, Sb	15
f	Electron deficient structures Ga_{12}^{12-}, $Tl@Tl_{12}^{10-}$	16, 17

Several examples of main group metal clusters of the above types modeled by the electronically equivalent Ge_n clusters were discussed in the full presentation at MOLMOD 2007 held in Arcalia/RO [22]. Here we provide a short account of the main results.

RESULTS AND DISCUSSION

There are numerous experimentally realized examples of bipyramidal M_n clusters with 2n+2 skeletal electrons, which we have used to check the validity of the computational method chosen for this study. Table 2 lists some of the geometrical parameters for such clusters, along with the computed values of the isoelectronic Ge clusters. These data show that the overall shape of the cluster (expressed through the ratio of the eq-eq/ax-eq distance) is well reproduced by computing and, at least for the purpose of this investigation, the B3LYP method is sufficiently reliable.

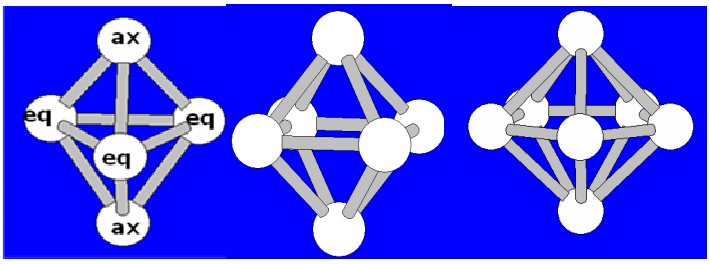

Figure 1. Three of the common bipyramidal structures encountered in cluster chemistry.

Table 2.

Relevant geometrical parameters for some bypiramidal clusters

Cluster	eq–eq	eq–ax	ax…ax	eq–eq/ ax–eq	Ref.
Ge_5^{2-}	2.818	2.577	3.997	1.09	23[e]
Ge_5^{2-}	2.68±0.02	2.49±0.03	3.90±0.02	1.08	24[c]
Sn_5^{2-}	3.238	3.002	4.70	1.08	25[e]
Pb_5^{2-}	3.095	2.877	4.49	1.08	25[e]
Bi_5^{3+}	3.326	3.013	4.646	1.10	26[e]
Tl_5^{7-}	3.280	3.214		1.02	27[e]
Tl_5^{7-}	3.32	3.15±0.01		1.05	28[e]
Ge_6^{2-}	2.687	2.687		1.00	23[c]
$[Ge_6\{Cr(CO)_5\}_6]^{2-}$	2.541	2.541		1.00	29[e]
Ge_7^{2-}				0.91	23[c]
$B_7Br_7^{2-}$				0.90	30[e]

[e]experimental data; [c]calculated data

Removal of two electrons from the Ge_n^{2-} clusters shown above leaves only 2n electrons for skeletal bonding. Various possibilities arise to compensate for these two missing electrons. One way is the flattening of the cluster so that two of the degree 4 vertices approach the center of the polyhedron with their otherwise external electron pairs thus becoming involved in the skeletal bonding (Figure 2). In the above Ge_n cases this deformation is observed as a shortening of the axial/axial Ge···Ge distances, in accord with the experimentally observed flattening of the isolobal and isoelectronic Tl_7^{7-} [31] or $Au_7(PPh_3)_7^+$ [32]

By decreasing the ax/ax distance, the population of the the external orbital bearing the lone pair of Ge in the Ge_n^{2-} cluster drops from values typically close to 2 down to 0.65 in Ge_5. Molecular orbitals of bipyramidal Ge_n^{2-} show that the HOMO is always Ge···Ge antibonding along the axial-axial direction, so the removal of two electrons from these orbitals increases the effective Ge···Ge bond orders thereby shortening these distances.

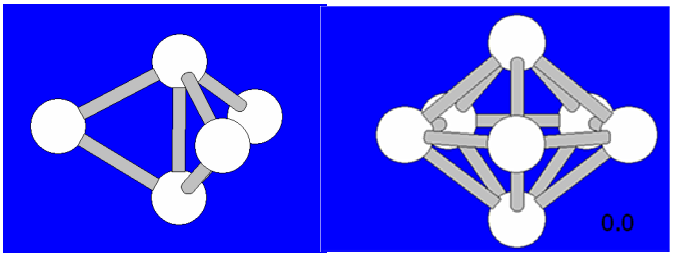

Figure 2. B3LYP/DFT optimized structures of Ge_5 and Ge_7

An interesting case occurs in Ge_8^{2-}, for which the global minimum is a tetracapped tetrahedron [33] rather than the bisdisphenoid expected from the Wade-Mingos rules (Figure 3). The other E_8^{2-} (E=Si, Ge, Sn) clusters also have a tetrahedral shape [34] in sharp contrast to the structure of the known **deltahedral borane** anion $B_8H_8^{2-}$ [35] and the isoelectronic neutral dicarbahexaborane $Me_2C_2B_6H_6$ [36], but in line with the **spherical (homo)aromatic** character assignable to the E_8^{2-} clusters [34].

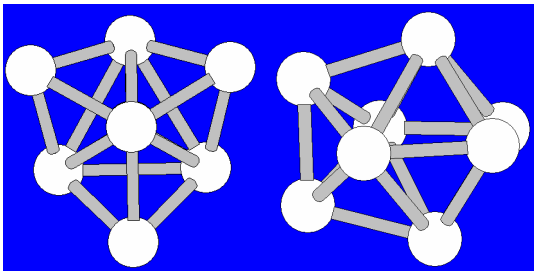

Figure 3. The lowest energy geometries of Ge_8^{2-}

Again, the occupation of the "lone pair" (LP) orbitals of the Ge atoms at the degree 6 vertices (forming the inner tetrahedron) drops to 0.69, as a result of a high degree of delocalization into the skeletal orbitals.

A similar violation of the Wade-Mingos rules has been noted for Ge_{11}^{2-}. Thus, $B_{11}H_{11}^{2-}$ is found both experimentally [37] and computationally [38] to have *a* C_{2v} edge-coalesced icosahedron structure whereas Ge_{11}^{2-} has a deformed pentacapped trigonal prism as its global minimum [38].

The eight- and eleven-vertex systems thus provide examples where lone pairs on Ge vertices versus hydrogen atoms on BH vertices make a significant difference in the relative stabilities of different polyhedral structures.

CONCLUSIONS

B3LYP/DFT calculations results on model $Ge_n^{z+/-}$ clusters focus on the influence of the external lone pairs of germanium atoms on the geometry of hypoelectronic and some of the electron precise clusters, providing thus rationale for the understanding the observed geometries of analogous systems.

EXPERIMENTAL SECTION

Hybrid B3LYP/6-311G* or Lanl2dz(d) calculations were carried out on Ge_n^z clusters (n=5-14) with z varying to cover a large variety of hypo- or hyperelectronic systems. The default fine grid in Gaussian 94 and Gaussian 98 [39,40]

was used for integration. In all cases we started from the highest symmetry allowed by a particular arrangement/connectivity. The nature of the optimized structures were checked by vibrational analysis. When imaginary frequencies were found, the corresponding normal modes were followed in order to locate the genuine minima.

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