Int.J.HIT.TRANSC:ECCN.Vol.4: Issue 1A (2018) Page 1-7 ISSN: 0973-6875

Available Online at www.hithaldia.in/locate/ECCN

ORIGINAL CONTRIBUTION

Ligand Driven Electron Counting Rule Selection: A Case Study for Ge_5R Complex

Rakesh Parida[1], G. Naaresh Reddy[1], Ajay Khanna[1], Gourisankar Roymahapatra[2] and Santanab Giri[1,*]

[1]*Theoretical Chemistry Laboratory, Department of Chemistry, National Institute of Technology Rourkela, India -769008*

[2]*Dept. of Applied Sciences, Haldia Institute of Technology, Haldia Knowledge City, Haldia-721657, WB, India*

(Received Date: 18th November, 2017; Acceptance Date: 15th February, 2018)

ABSTRACT

Density Functional Theory based calculations of Zintl complex Ge_5R, proposed that it is possible to anticipate which electron-counting rule will be suitable for the examination of stability of Zintl complex. The two prominent electron-counting rules have been taken into consideration, Jellium shell closer model and Wade-Mingos rule. Upon thorough analysis, we have observed that, if the ligand is electron donating, the Jellium shell closer model describes complex stability and electron withdrawing ligand leads to Wade-Mingos rule to describes the stability of the Zintl complex, Ge_5R.

Keywords: Cluster, Electron affinity, Ionization energy, Electron counting rules.

1. INTRODUCTION

Electron counting rules[1-4] plays a significant role in chemistry. They help in anticipating the stability of the molecules, complexes, metal clusters[5,6] etc. Depending on the nature of the molecules, we have various electron counting rules e.g. the well-known Octet rule[7] which is suitable for main group elements, while 18 electron rule[4,8-11]accounts for the stability of the transition metals and its complexes. In spite of these electrons counting rules, there are other electron counting rules developed time to time to analyze the stability of different molecules and complexes. The renowned Jellium shell closer model[12,13] and Wade-Mingos rule[14-17]are two among those other rules. The Jellium model had its origin in nuclear physics and first applied to gas phase clusters. The magic numbers of this model that leads to stability of the systems that includes 2, 8, 18, 20, 34, 40…. electrons. The superatom[18-24]behaviour of Al_{13}-cluster can be explained by Jellium shell closer model. According to this model the electronic configuration is $1s^2\ 1p^6\ 1d^{10}\ 2s^2\ 1f^{14}\ 2p^6$….. which is different from the Aufbau principle[25]. On the other hand, Wade-Mingos rule follows 4n+2, 4n+4, 4n+6 pattern to form closo, nido, arachno based polyhedral cluster respectively, where n is the number of vertices of the cluster. The stability of Ge_9^{2-} cluster[26-27] which is a 38 valance electron system is explained only by Wade-Mingos rule as it follows the 4n+2 pattern whereas, the stability of Ge_9^{4-} cluster[28-29] is explained by both Jellium and Wade-Mingos rule due to 40 electron system. Thus we can see that these electron counting rules can be implemented individually or simultaneously to foretell the stability of the complexes. In the manuscript we want to see which electronic counting rule will be applicable to predict the stability of a Germanium-based Zintl complex Ge_5R where R act as some electron donating group (EDG) like $-NH_2$, -OH, $-NHCOCH_3$, $-OCOCH_3$, $-CH_3$, -Ph, $-(CH=C(CH)_3)_2$, and electron withdrawing group (EWG) as –F, -Cl, -Br, -CHO, -COCl, $-CF_3$, -CN, $-SO_3H$, $-NO_2$. Here, Ge_5 is a 20 valence electron system and we assume that each R will give one electron to the core,(when the ligand R coordinate with Ge_5

*Corresponding Address: giris@nitrkl.ac.in

cluster by one of equatorial Ge atom leads to the formation of Ge_5R) leading to the formation of Ge_5R in which , 21 electrons take part in the bonding. According to any electronic counting rule it is not a stable electronic configuration. Now to gain the stability, Ge_5R complex can take either one additional electron to have 22 electrons or it can lose one electron and becomes 20 electron system. According to the Wade-Mingos and Jellium rule, both 22 and 20 are stable electron configuration respectively. We assume that the nature of the R will play a significant role in selecting the electron-counting rule. If R is an electron-donating group, then electron density inside the core Ge_5 will be high. To maintain the stability, the complex will eject one electron. So 21 electronic system becomes 20 electron system and thus Jellium shell closer model can explain its stability. The situation will be reverse when the nature of the R will be electron withdrawing. In this case, the complex will take an additional electron. So in the complex 22 electrons will take part in the bonding. This which can be explained by Wade-Mingos rule. In this manuscript we have investigated this idea and try to give a general explanation that helps to select the electron-counting rule for the account of stability of Germanium complex.

Objectives

- To understand effect of ligand on the Ge_5R complex.
- Detailed study of Jellium shell closer model and Wade-Mingos rule in the help of EDG and EWG.

2. COMPUTATIONAL DETAILS

To investigate our idea, we have optimized all model Ge_5R (R=EWG/ERG) clusters to have ground state electronic structure. In Ge_5^{2-} cluster[30] two positions are suitable for ligand substitution, axial and equatorial. So we have optimized all the axial and equatorial isomers by employing wB97XD[31] level of theory with 6-31+G(d,p) as basis set. In addition, we have performed the vibrational frequency calculation by using same level of theory and basis set. In every cases zero imaginary frequencies indicate that all the investigated systems are at local minima on their respective potential energy surfaces. Further to obtain the electron affinity (EA) and ionization energy (IE) we have optimized their corresponding cations and anions. From the energy difference of the cation, neutral and anion, we have calculated the EA and IE. We have performed NBO[32] analysis to get Wiberg bond index values, charge distribution pattern and electron population distribution. In addition to NBO analysis, we have calculated the Laplacian of electron density, bond critical point between two atoms to see whether the ligands are really sharing their valance electrons with the Core Ge_5. A 2c-2e bonds are also analyzed by Adaptive Natural Density Partitioning (AdNDP)[33] method. All the calculations were carried out utilizing the Gaussian 09W[34] software and multiwfn[35] software.

3. RESULTS AND DISCUSSION

As mentioned earlier, we have assumed that the ligands are sharing one valance electron with Ge_5 core to form Ge_5R complex, we have taken three different ligands NH_2, NO_2 and CH_3 to make sure that they indeed sharing one electron to make Ge_5R (R= NH_2, NO_2 and CH_3) complex where 21 electrons will be the number of bonding electrons. The optimized ground state geometries are given in Figure 1. We have noticed that, the equatorial isomer is more stable than axial isomer. The Wiberg bond index calculated from NBO analysis are given along with the optimized geometries. We have found that, the bond index values between Ge and N atom for Ge_5NH_2 is 0.785 whereas for CH_3 and NO_2 it is 0.853 and 0.565 respectively. This suggests that there is an indication of bond formation between Ge and N/C atoms. To investigate further, we have generated the covalent character of the complex, contour map of electron density Laplacian along with bond critical points. The corresponding figures are given in Figure 2. Positive and negative electron densities are denoted as solid and dashed lines respectively. The electron density contour suggests that there is an interaction between atom involved in bonding. We have also found a bond critical point between Ge and N/C atoms.

This indicates that ligands are forming bonds with Ge_5 cluster to produce Ge_5R complex. For further clarification we have performed a 2c-2e bond analysis between Ge and N/C atoms by AdNDP methodology. The 2c-2e bonds are presented in Figure 3. The occupancy number for all three cases is 1.99|e| which indicates the presence of a bond between Ge and N/C atoms of the ligands via electron sharing. From the above analysis we can assume that 21 electrons (Core : 20 ligand : 1) are taking part in bonding. To confirm the number, we have seen the natural electron configuration and natural electron population after bond formation between the Ge_5 and the NH_2 and NO_2, which has been shown in Table 1 and Table 2 respectively.

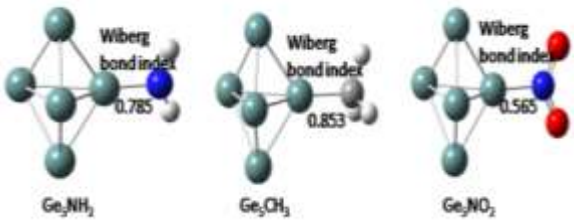

Figure 1: Wiberg bond index in NAO basis between Ge, N of Ge_5NH_2 and Ge_5NO_2 and Ge, C of Ge_5CH_3

From the NBO analysis we have found that the population of Ge_5 is approximately 20. When this Ge_5 forms bond with NH_2 then the population of core Ge_5 decreases to 19.26. That suggests, the remaining electrons are taking part in the formation of the bond between Ge-N. From 2c-2e analysis we confirmed that, two electrons are involved in the formation of the bond. So the overall bonding electron population in Ge_5-N is approximately 21 (Core: ~19; Ge-N: 2). The same is obtained for $[Ge_5NH_2]^+$ and $[Ge_5NH_2]^-$. In $[Ge_5NH_2]^+$, $[Ge_5NH_2]^-$ the population of core Ge_5 is 18.39 and 20.25 respectively and the overall population is approximately 20 for cation and 22 for anion complex.

Similarly, we have found in $[Ge_5NO_2]$ the natural population core Ge_5 is 19.45 and the extra electron involved in 2c-2e bond formation between Ge_5-N. So, we can say that the overall population is approximately 21 in this complex.

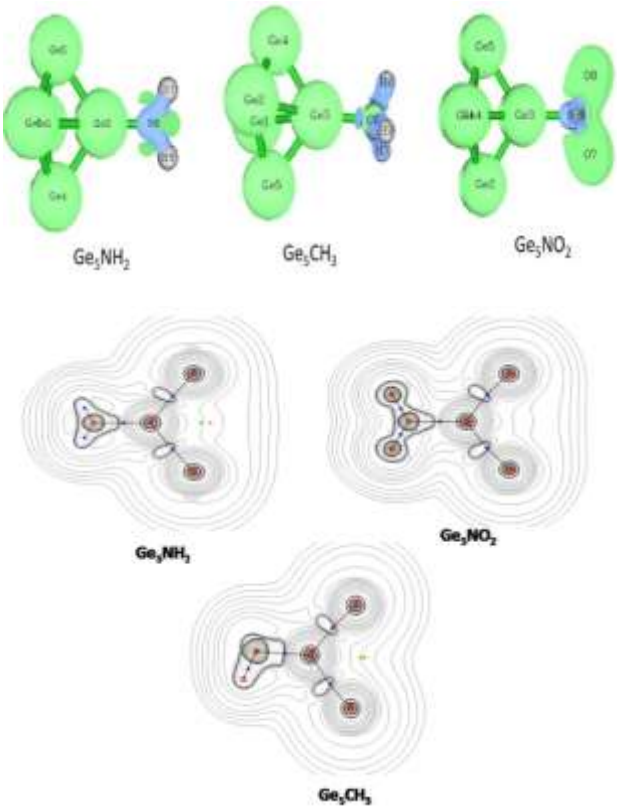

Figure 2: Colour and Contour map of electron density laplacian of Ge_5NH_2 , Ge_5CH_3, Ge_5NO_2; On the plane containing three axial Ge and N in both the case;(3,-1) Bond critical point (blue), (3,-3) Nuclear Critical point (orange) with topology paths; Positive and negative values are denoted by solid and dashed line respectively

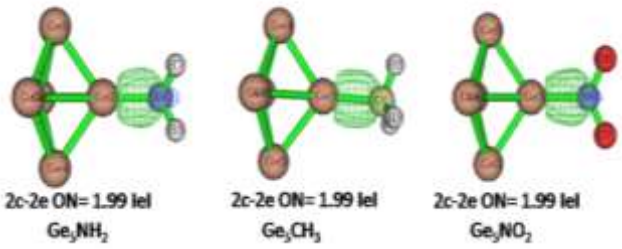

Figure 3: 2c-2e bond between Ge and R of Ge_5NH_2, Ge_5CH_3 and Ge_5NO_2 with occupation number (ON)

Again in $[Ge_5NO_2]^+$, $[Ge_5NO_2]^-$ the population of core Ge_5 is 18.39 and 20.18 respectively. So the overall population is approximately 20 and 22 for cation and anion complex respectively. Now it is important to know which stable electron system will be adopted by the neutral complex.

Table 1: Valence electron configuration of Ge_5NH_2 and Ge_5NO_2 from NBO analysis

Atom with label	**Ge_5NH_2**	**Ge_5NO_2**
Ge1	4S(1.76)4p(2.11)4d(0.3) 5p (0.1)	4S(1.77)4p(2.07)4d(0.03) 5p(0.01)
Ge2	4S(1.17)4p(2.40)5S(0.0) 4d(0.04) 5p(0.01)	4S(1.69)4p(2.19)4d(0.04) 5p(0.01)
Ge3	4S(1.76)4p(2.12)4d(0.3) 5p(0.01)	4S(1.28)4p(2.57)4d(0.05) 5p(0.02)
Ge4	4S(1.67)4p(2.33)4d(0.4) 5p (0.01)	4S(1.77)4p(2.07)4d(0.03) 5p(0.01)
Ge5	4S(1.67)4p(2.33)4d(0.4) 5p(0.1)	4S(1.69)4p(2.19)4d(0.04) 5p(0.01)
N	2S(1.48)2p(4.80)3p(0.1)	2S(1.22)2p(3.42)3S(0.02) 3p(0.03)3d(0.02)4p(0.01)

Table 2: Natural electron population of Ge_5NH_2 and Ge_5NO_2 from NBO analysis

Natural electron population					
Ge_5NH_2			Ge_5NO_2		
Atoms	Neutral	Cation	Atoms	Neutral	Anion
Ge_1	3.88	3.49	Ge_1	3.83	4.07
Ge_2	3.56	3.24	Ge_2	3.88	4.08
Ge_3	3.89	3.49	Ge_3	3.84	3.88
Ge_4	4.0	4.09	Ge_4	3.83	4.07
Ge_5	4.0	4.09	Ge_5	3.88	4.08
N	6.28	6.28	N	4.63	4.62
H	0.56	0.53	O	6.35	6.40
H	0.56	0.53	O	6.35	6.40

In the case of Ge_5NH_2, NH_2 is acting as an activating group, and it can donate electrons to the Ge_5 cluster.

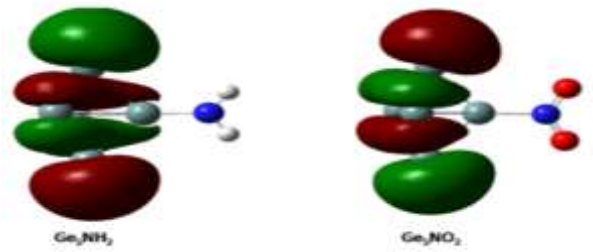

Figure 4: Highest Occupied Molecular Orbital of Ge_5NH_2 and Ge_5NO_2

So the electron density inside the cluster increases. Reverse will happen in case of a deactivating group like NO_2. In this case electron density will be less. To account that we have generated the frontier molecular orbitals, mainly HOMO. The corresponding HOMO's are given in Figure 4.

From Figure 4 it can be visualized that electron density over the three membered ring of Ge_5 cluster is high in the case of NH_2 than NO_2. If this is the case, the electron affinity of Ge_5R having activating/deactivating groups will be less/high. In other word ionization potential of Ge_5R having activating/deactivating groups will also be less/high. To explain this, we have calculated the EA and IE of these complexes and found that the EA (IE) of Ge_5NH_2 is 2.625 eV (6.755 eV) whereas for Ge_5NO_2 it is 3.288 eV (7.699 eV). This suggests that Ge_5NH_2can easily release an electron to have the stable electronic structure as $[Ge_5NH_2]^+$ in which there will is approximately 20 bonding electron as found in NBO analysis. Now the stability can be explained by Jellium shell closer model. But The situation is reversed in the case of Ge_5NO_2. It wants to get stabilized by receiving an extra electron to form 22 electron system, $[Ge_5NO_2]^-$ which can be explained by the Wade-Mingos rule.

After having these results, we have modeled the rest of the complexes with all possible isomers. The optimized geometries of Ge_5R complexes are given in Figure 5. and Figure 6.

In Figure 5, R is electron donating group whereas in Figure 6, R is electron withdrawing in nature. Most of the cases we have found that

equatorial position is most preferable than axial for ligand substitution. The energy differences between two isomers are also given in Figures 5 and 6. As for example equatorial Ge_5NH_2, Ge_5CH_3 are 0.05 eV more stable than its correspond axial isomers. For ligand Ph, equatorial complex is 0.27 eV more stable than axial.

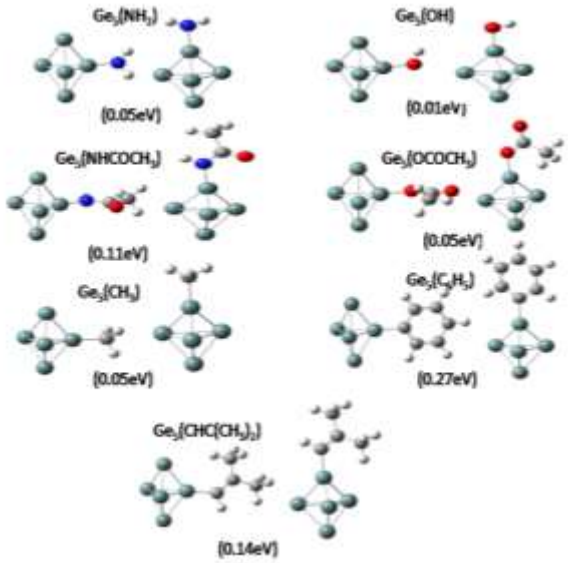

Figure 5: Optimized geometries of different Ge_5R (R=EDG) complexes with energy difference

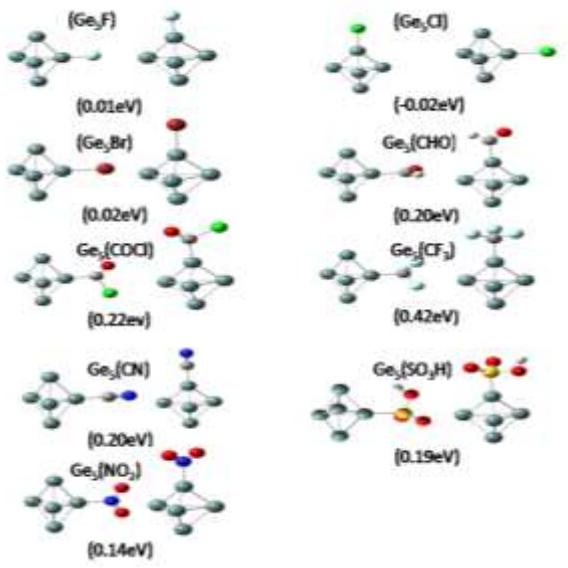

Figure 6: Optimized geometries of different Ge_5R (R=EWG) complexes with energy difference

The situation is reversed when the ligand is Cl. Here axial Ge_5Cl is more stable than equatorial complex by 0.02 eV. Now the question is which selection rule we can apply for these complexes to describe the stability. The tendency of taking or releasing electron can be determined by calculating the electron affinity (EA) and ionization energy (IE) respectively. The calculated electron affinity and ionization energy values of these Ge_5R complexes are shown in Table 3 and Table 4 respectively.

Table 3: Calculated Electron affinity of different Ge_5R complexes

Compound	EA (eV)	Compound	EA (eV)
$Ge_5(NH_2)$	2.625	Ge_5F	2.970
$Ge_5(OH)$	2.798	Ge_5Cl*	3.317
$Ge_5(NHCOCH_3)$	2.782	Ge_5Br	3.001
$Ge_5(OCOCH_3)$	3.222	$Ge_5(CHO)$	2.980
$Ge_5(CH_3)$	2.587	$Ge_5(COCl)$	3.161
$Ge_5(C_6H_5)$	2.724	$Ge_5(CF_3)$	3.049
$Ge_5(CHC(CH_3)_2)$	2.607	$Ge_5(CN)$	3.216
Ge_5H	2.708	$Ge_5(SO_3H)$	3.399
		$Ge_5(NO_2)$	3.288

Table 4: Calculated Ionisation Energy of different Ge_5R complexes

Compound	IE (eV)	Compound	IE (eV)
$Ge_5(NH_2)$	6.755	Ge_5F	7.335
$Ge_5(OH)$	7.05	Ge_5Cl*	7.268
$Ge_5(NHCOCH_3)$	6.293	Ge_5Br	7.238
$Ge_5(OCOCH_3)$	7.031	$Ge_5(CHO)$	7.22
$Ge_5(CH_3)$	6.848	$Ge_5(COCl)$	7.462
$Ge_5(C_6H_5)$	6.813	$Ge_5(CF_3)$	7.442
$Ge_5(CHC(CH_3)_2)$	6.7	$Ge_5(CN)$	7.634
Ge_5H	7.047	$Ge_5(SO_3H)$	7.517
		$Ge_5(NO_2)$	7.699

From the table, we can observe that in the presence of electron donating group the EA values are less whereas it is high for electron withdrawing group. This implies that the system is not willing to take additional electron, rather releasing electron to gain stability.

4. CONCLUSIONS

By relating all the theoretical data and explanation, we can conclude that ligands are sharing electron to form complex and nature of the ligand leads to different electron counting rule to explain the stability. Electron releasing group ended up with Jellium shell closer model whereas Wade-Mingos rule is associated with the electron withdrawing nature of the ligand.

Acknowledgement

This work is funded by the Department of Science and Technology (DST), Government of India, INSPIRE award no IFA14-CH-151. Resources and computational facilities of National Institute of Technology Rourkela are also greatly acknowledged.

References

[1] Rasmussen, S. C. (2015). The 18-Electron Rule and Electron Counting in Transition Metal Compounds: Theory and Application, Chem. Texts. (1) 1-10.

[2] Teo, B. K. A. (1983). Simple Electron Counting Rule for Close-packed High Nuclearity Metal Clusters. J. Chem. Soc., Chem. Comm. (0) 1362-1364.

[3] Bose, D. M. (1926). Valence Theories and the Magnetic Properties of Complex Salts Nature. (117) 84-84.

[4] Zhou, J. Giri, S. Jena, P. (2014). 18-Electron rule inspired Zintl-like ions Composed of All Transition Metals**.** Phys. Chem. Chem. Phys. (16) 20241-20247.

[5] Morse, M. D. (1986). Clusters of Transition-Metal Atoms.Chem. Rev. (86) 1049-1109.

[6] Christen, W.W. and Even, U. (1998) Cluster Impact Chemistry. J. Phys. Chem. A. (102) 9420-9426.

[7] Noury, S. Silvi, B. (2002). Chemical Bonding in Hypervalent Molecules: Is the Octet Rule Relevant? Inorg. Chem. (41) 2164-2172

[8] Auvert, G. (2014). Improvement of the Lewis-Abegg-Octet Rule Using an "Even-Odd" Rule in Chemical Structural Formulas: Application to Hypo and Hyper-Valences of Stable Uncharged Gaseous Single-Bonded Molecules with Main Group Elements. Open J. Phys. Chem. (4) 60-66.

[9] Jensen, W. B. (2005). The Origin of the Bunsen Burner.J. Chem. Edu. (82) 518.

[10] Sidgwick, N. V. (1927) The Electronic Theory of Valency; Clarendon Press: Oxford,.

[11] Mitchell, P. R. Parish, J. (1969). The Eighteen Electron Rule.J. Chem. Edu. (46) 811-814.

[12] Koskinen, M. Lipas, P. O. and Manninen, M. (1995) Electron-gas Clusters: the Ultimate Jellium Model. Z. Phys. D. (35) 285-297.

[13] Bauer, D. (2012) Modeling the Core-hole Screening in Jellium Clusters Using Density Functional Theory. New J. Phys. (14) 055012.

[14] Sevov, S. C. Westbrook, J. H. and Eds. Freisher, R. L. (2002) Zintl Phases In Intermetallic Compounds, Principles and Practice: Progress; John Wiley & Sons. Ltd.: Chichester, England.

[15] Mandal, S. Liu, R .Reber, A. C Qian, M. Saavedra, H. M. Ke, X. Schiffer, P. Sen, S. Weiss, P. S. Khanna, S. N. and Sen, A. (2011). The Zintl ion $[As_7]^{2-}$: An Example of an Electron-Deficient As_x Radical Anion. Chem. Comm. (47) 3126-3128.

[16] Zhenyang, L. Slee, T. and Mingos, D. M. P. (1990). A Structural Jellium Model of Cluster Electronic Structure. Chem. Phys. (142) 321-334.

[17] Wade, K. (1971). The Structural Significance of the Number of Skeletal Bonding Electron Pairs in Carboranes, the Higher Boranes and Borane Anions, and Various Transition Metal Carbonyl Cluster Compounds. Chem. Comm (0) 792-793.

[18] Han, Y. K. and Jung, J. (2008) Does the "Superatom" Exist in Halogenated Aluminum Clusters? J. Am. Chem. Soc. (130) 1-3.

[19] Bergeron, D. E. Roach, P. J. Castleman, A. W. Jr. Jones, N. O. Khanna, S. N. (2005). Al Cluster Superatoms as Halogens in Polyhalides and as Alkaline Earths in Iodide Salts,Science, (307) 231-235.

[20] Sun, W. M. Wu, D. Li, X. H. Li, Y. Chen, J. H. Li, C. Y. and Liu, J. Y. (2016). Quasi-Chalcogen Characteristics of $Al_{12}Be$: A New Member of the Three-Dimensional Periodic Table.J. Phys. Chem. C. (120) 2464−2471.

[21] Reveles, J. U. Baruah, T. and Zope, R. R. (2015). $Al_{12}Cu$ Superatom as Stable Building Block of Ionic Salts. J. Phys. Chem. C. (119) 5129-5137.

[22] Champsaur, M. Velian, A. Paley, D. W. Choi, B. Roy, X. Steigerwald, M. L. and Nuckolls, C. (2016) Building Diatomic and Triatomic Superatom Molecules.Nano Lett. (16) 5273-5277.

[23] Zhang, X. Wang, Y. Wang, H. Lim, A. Gantefoer, G. Bowen, K. H. Reveles, J. U. and Khanna, S. N. (2013). On the Existence of Designer Magnetic Superatoms. J. Am. Chem. Soc. (135) 4856-4861.

[24] Reveles, J. U. Clayborne, P. A. Reber, A. C. Khanna, S. N. Pradhan, K. Sen, P. and Pederson, M. R. (2009). Designer Magnetic Superatoms. Nat. Chem. (1) 310-315.

[25] Vanquickenborne, L. G. Pierloot, K. and Devoghel, D. (1994). Transition Metals and the Aufbau Principle. J. Chem. Edu. (71) 469-471.

[26] Scharfe, S. and Fassler, T. F. Phil. (2010) Polyhedral Nine-atom Clusters of Tetrel Elements and Intermetalloid Derivatives. Trans. R. Soc. A. (368) 1265–1284.

[27] Ugrinov, A. and Sevov, S. C. (2002) $[Ph_2Bi{-}(Ge_9){-}BiPh_2]^{2-}$: A Deltahedral Zintl Ion Functionalized by Exo-Bonded Ligands. J. Am. Chem. Soc. (124) 2442-2443.

[28] Xu, L. and Sevov, S. C. (1999). Oxidative Coupling of Deltahedral $[Ge_9]^{4-}$ Zintl Ions. J. Am. Chem. Soc. (121) 9245-9246.

[29] Cabrera, W. C. Gila, R. C. Somerb, M. Persilb, Ö. And Schneringc, H. G. V. (2003). $Na_{12}Ge_{17}$: A Compound with the Zintl Anions $[Ge_4]^{4-}$ and $[Ge_9]^{4-}$ Synthesis, Crystal Structure, and Raman Spectrum. Z. Anorg. Allg. Chem., (629) 601-608.

[30] Campbell, J. Schrobilgen, G. J. (1997). The *closo*-Ge_5^{2-} Anion: Synthesis, Crystal Structure, and Raman Spectrum of (2,2,2-crypt-$K^+)_2Ge_5^{2-}$·THF. Inorg. Chem., (36) 4078-4081.

[31] Chai, D. and Head-Gordon, (2008) M. Long-range Corrected Hybrid Density Functionals with Damped Atom–Atom Dispersion Corrections. Phys. Chem. Chem. Phys., (10) 6615-6620.

[32] Reed, A. E. Curtiss, L. A. And Weinhold, F. (1988). Intermolecular interactions from a natural bond orbital, donor-acceptor viewpoint. Chem. Rev. (88) 899-926

[33] Zubarev, D. Y. And Boldyrev, A. I. (2008). Developing Paradigms of Chemical Bonding: Adaptive Natural Density Partitioning. Phys. Chem. Chem. Phys.(10) 5207–5217.

[34] Frisch, M. J. Trucks, G. W. Schlegel, H. B. Scuseria, G. E. Robb, M. A. Cheeseman, J. R. Scalmani, G. Barone, V. Mennucci, B. Petersson, G. A. et al. (2010). Gaussian 09, revision B.01; Gaussian, Inc.: Wallingford, CT.

[35] Lu, T. And Chen, F. (2012). Multiwfn: a multifunctional wavefunction analyzer. J. Comput. Chem. (33) 580–592.