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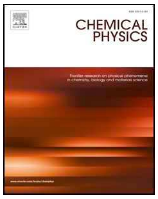

Two names of stability: Spherical aromatic or superatomic intermetalloid cluster $[Pd_3Sn_8Bi_6]^{4-}$

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A B S T R A C T

Amidst the general bonding patterns designed to explain stability aromaticity has leading role. Going far away beyond classic notion of organic chemistry aromaticity was proven to be a useful tool to decipher stability of many clusters, all-metal compounds and solid states. Here we present chemical bonding model for recently synthesized highly aesthetic intermetalloid cluster $[Pd_3Sn_8Bi_6]^{4-}$. We found pattern based on spherical aromaticity consistent with Hirsch $2(n + 1)^2$ rule and responsible for bonding of Pd_3 internal triangle to the external Sn-Bi cage. Spherical aromatic clusters are also referred as superatoms and due to their persistency are of primary interest for material science and nanotechnology. We also included brief guidelines how to decipher bonding pattern in complicated cases like $[Pd_3Sn_8Bi_6]^{4-}$ into SI.

1. Introduction

Chemical society has been seeking for the general bonding patterns and rules which could explain stability or reactivity of non-trivial compounds for many years. Aromaticity proved itself as one of the most remarkable and useful concepts which has been existing for more than one century [1–4]. Expansion of aromaticity on wide variety of systems led to the remarkable dispute in scientific community after Hoffman critical review was published [5,6]. Game changing study by Saito and coworkers laid a new milestone in this debate since they managed to obtain π- and σ-aromatic compound $[C_6(SePh)_6]^{2+}$ experimentally [7]. Its aromaticity was shown not only by calculations but also supported by experimental data such a magnetic response, X-ray analysis and EPR. This is indeed a breakthrough in aromaticity debate which adds new solid evidences that σ-aromaticity is not elusive. These advances obviously indicate that paradigms of aromaticity are expanding right now and they should go beyond classic notion and organic chemistry [3]. Remarkably, elegant ideas of aromaticity and antiaromaticity was successfully applied to decipher chemical bonding in many clusters [8–18], Zintl phases [19–21] and all-metal compounds [22–24]. Nevertheless, intermetalloid clusters per se are the most complicated cases for bonding analysis since they are electron-deficient meaning that their real bonding cannot be simply represented by Lewis structural formulas familiar to any chemist. Moreover, electron deficient character of such systems alongside with their stability give us a hint to look for aromaticity.

Exciting example is intermetalloid cluster $[Pd_3Sn_8Bi_6]^{4-}$ synthesized in a solid phase few years ago by Dehnen and coworkers (Fig. 1) [25]. This promising cluster is of great interest since this is a bottleable compound which stability is not under any doubts and the structure was already designed by the mother nature. Attracted by this unusual highly aesthetic system we performed its bonding study and recovered pattern based on spherical aromaticity. Along with σ-aromaticity spherical aromaticity is relatively young approach. Firstly Lipscomb started calling this phenomenon superaromaticity [26] but then society switched to the term 3D aromaticity [27,28]. Modern notion of spherical aromaticity was born during fullerenes stability exploration [29–31] and then was expanded to 3D systems formed from the other elements [12,13,30,32]. While stability of planar systems such as canonical benzene could be explained within Huckel's rule $4n + 2$, for 3D or spherical system Hirsch rule $2(n + 1)^2$ is applicable and that is the case of $[Pd_3Sn_8Bi_6]^{4-}$ which we will discuss further.

Up to date two interesting interpretations of chemical bonding in $[Pd_3Sn_8Bi_6]^{4-}$ were suggested. One was developed in original work [25] and used CMO and LMO approach to determine how Pd_3 cage contributes to the overall bonding picture and which bonds hold $[Pd_3Sn_8Bi_6]^{4-}$ as an entity. However, authors agreed that pattern was not solved completely and none of the models considered do not describe the true structure of $[Pd_3Sn_8Bi_6]^{4-}$ cluster. The same question about plausible bonding in this intermetalloid cluster was raised in the recent paper by Zhai and coworkers [33]. They proposed alternative view and claimed multifold aromaticity (π and σ) as the main factor of

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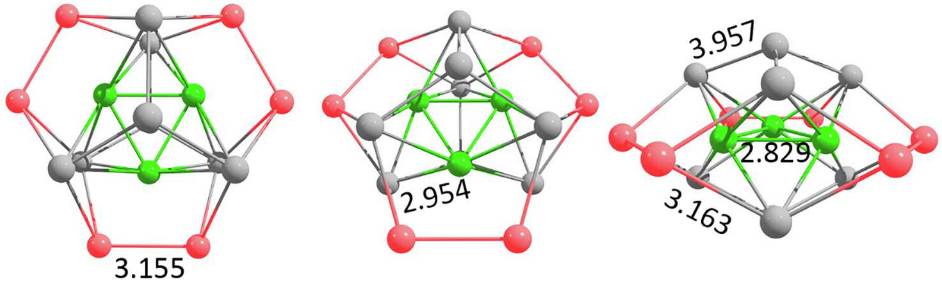

Fig. 1. Structure of $[Pd_3Sn_8Bi_6]^{4-}$ cluster obtained at the MN15L/Def2-TZVPP level of theory. Point group is D_{3h}. Hereinafter Bi atoms are red, Sn atoms are grey and Pd atoms are green. Lines linking atoms do not necessarily mean direct bonds and were added to improve readability of the picture. Bond lengths are given in Å.

stability. In our study we found new pattern explained in terms of spherical aromaticity or superatoms [13,34–37]. It is common for chemical bonding issues to have several possible interpretations. Bonding pictures in intermetalloid clusters are still actively disputed and we feel that even in case of $[Pd_3Sn_8Bi_6]^{4-}$ it is not settled yet. That is why we believe that our study may deepen not only the comprehension of this particular cluster but be helpful for the understanding of intermetalloid cluster bonding in general.

2. Results and discussion

To perform chemical bonding analysis according to the AdNDP method the most stable isomer from original work [25] was taken and optimized at the MN15L/Def2-TZVPP [38–40] level of theory. The equilibrium geometry belongs to D_{3h} point group and is in good consistency with the one reported in recent study [33]. Valence shell of $[Pd_3Sn_8Bi_6]^{4-}$ consists of 96 electrons: 30 coming from three Pd atoms, 32 from Sn and 30 from Bi which in sum with 4 additional electrons gives us 48 electron pairs.

With the aim of recovering the chemical bonding, general procedure of AdNDP [41,42] was applied starting with the 1c-2e bonds. As it was expected, we found five *d* orbitals on each Pd atom (Fig. 2), six lone pairs of *s* type on Bi atoms and eight on Sn atoms. To some extent this result is in the agreement with the NBO analysis [43–45] which also revealed lone pairs mostly of *s* character (80%) on each Bi atom. However, NBO failed dealing with lone pairs on Sn since on each Sn atom it showed two lone pairs. One of *s* type with the reasonable ON = 1.71|e| and the second one of *p* type with the ON = 0.78|e|. Additionally, two more orbitals on two Sn atoms were recovered both with the same ON = 0.73|e|. All these data indicate that NBO method could find only symmetry broken solution, hence it is not suitable for such complicated cases as $[Pd_3Sn_8Bi_6]^{4-}$. Nevertheless, all fifteen *d* orbitals belonging to three Pd atoms were obtained.

After that, according to the AdNDP method, set of 2c-2e bonds directly linking Bi-Bi atoms and Sn-Sn was found with the ON = 1.80 and 1.67|e|, respectively. Now it is clear that exactly 2c-2e σ-bonds are responsible for the internal UFO-shaped cage formation. The same results could be obtained within NBO approach making sense since NBO usually recover strongly localized bonds well. Meantime, no other bonds were found using NBO approach and residual density was represented only by Rydberg natural bonds having unacceptably low ON which as a rule indicates multicenter character of undistributed density.

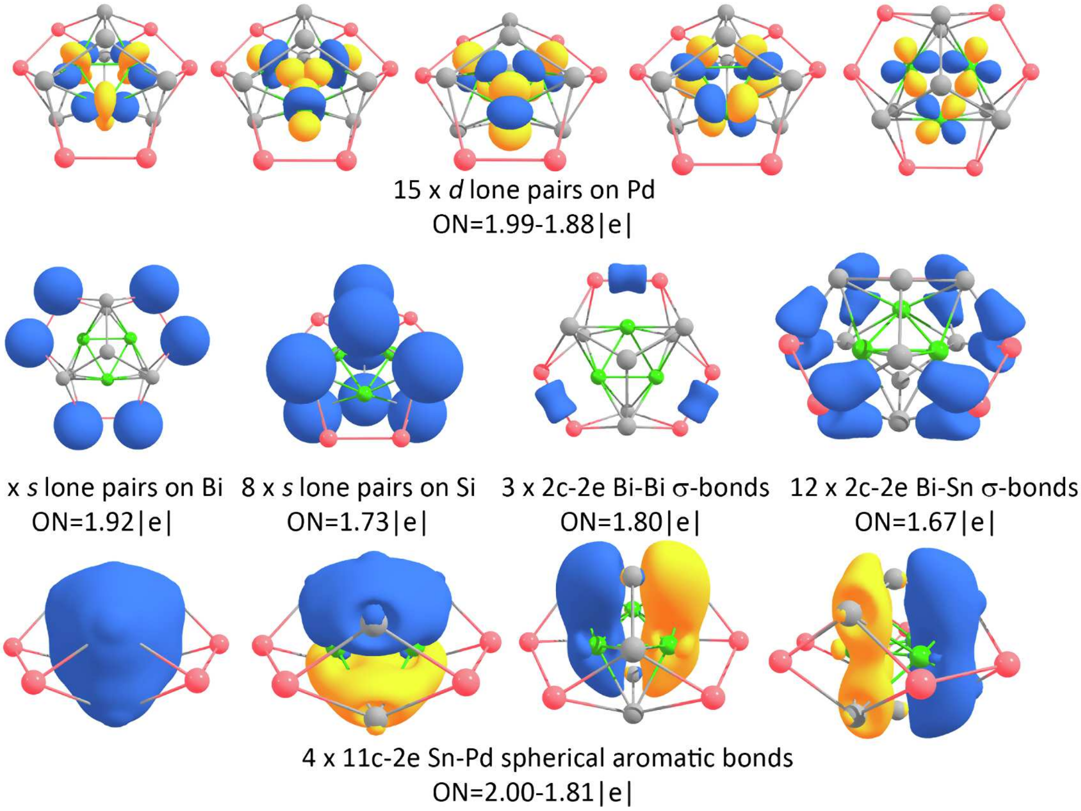

Fig. 2. Bonding pattern of $[Pd_3Sn_8Bi_6]^{4-}$ cluster obtained by the AdNDP method. Lines linking atoms do not necessarily mean direct bonds and were added to improve readability of the picture.

At this point, according to the AdNDP method, only four electron pairs remained unrecovered thus giving us clue that residual density might comply with Hirsch rule $2(n+1)^2$. Indeed, we located four 11c-2e bonds involving all eight Sn and three Pd atoms. Starting with the bond without any nodal planes and then having three bonds with only one nodal plane this set indeed represents spherical aromaticity from both perspectives of electron counting rule $2(n+1)^2$ and shape of bonds.

Another important question regarding $[Pd_3Sn_8Bi_6]^{4-}$ is how Pd_3 triangle contributes to the overall structure. In order to enlighten role of Pd atoms we excluded neutral Pd_3 fragment and performed AdNDP on hollow $[Sn_8Bi_6]^{4-}$ cage without cluster reoptimization. Remarkably $[Sn_8Bi_6]^{4-}$ is still spherical aromatic structure and its overall bonding picture does not have any pronounced difference comparing to parental $[Pd_3Sn_8Bi_6]^{4-}$ (See Fig. S1). After that, we reoptimized $[Sn_8Bi_6]^{4-}$ cluster and Pd_3 fragment separately and, surprisingly, they turned out to be local minima. To validate these results and avoid any DFT-inaccuracies we also optimized both structures using time-tested PBE0 functional [46] and got the same data. Does it mean that we are dealing in this case not with fully bonded cluster but with inclusion compound? We believe that this structure should be considered as cluster since, according to the NBO data, each Pd bears negative charge 1.094|e| indicating sustainable charge transfer. Obviously, that Pd empty $5s^05p^0$ shell is responsible for the acceptance of the negative charge, therefore, encapsulated Pd_3 triangle has a role of charge aggregator stabilizing the whole system. However, realistic bonding picture of $[Sn_8Bi_6]^{4-}$ based on spherical aromaticity could be reached only using sophisticated combination of general and direct (also known as fragmented) AdNDP and we placed that discussion into SI as short but useful guideline for those who might be interested.

3. Conclusions

As we found using the AdNDP approach, complete picture of chemical bonding describes $[Pd_3Sn_8Bi_6]^{4-}$ structure as two-cage cluster in which internal Pd_3 fragment is bonded to the external cage by spherical aromatic bonds. These results are in full consistency with Hirsch $2(n+2)^2$ rule [30–32]. Localized bonds also agree to some extent to the classical NBO analysis, however the latter one could only reveal symmetry broken solution and could not recover crucial multicenter bonds responsible for holding all the atoms as entity. We consider this result as one more example proving usefulness of AdNDP method application to the intermetalloid clusters in which canonical MO are usually indecipherable. We believe that conundrum of $[Pd_3Sn_8Bi_6]^{4-}$ is finally solved and our findings are important for further understanding of intermetalloid clusters embedded with heavy metals. Noticeably that structures possessing spherical aromaticity sometimes are interchangeably referred as superatoms [13,34–36] and are of great interest for material science and nanotechnology within which they are considered as scalable and persistent building blocks [15,47–49].

4. Computational section

All quantum-chemical calculations were performed in Gaussian 16 software package [50]. Geometry of the most stable $[Pd_3Sn_8Bi_6]^{4-}$ isomer was taken from the original study [25] where exhaustive search out of 292 possible structures was carried out. Then it was reoptimized using newly developed highly accurate for heavy metals functional MN15-L [38] with the combination of redefined Ahlrichs triple-valence basis set Def2-TZVPP [39,40]. Separated $[Sn_8Bi_6]^{4-}$ and Pd_3 fragments were reoptimized at the same level of theory. Optimized structures were found to be energy minima, according to the frequency calculations. Additionally, it was checked using PBE0 functional and no significant differences were found. Chemical bonding pattern was recovered using both NBO analysis [43–45] and its recent extension known as AdNDP [41,42] at the PBE0/Def2-TZVPP level of theory.

Acknowledgments

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Conflict of interest

There are no conflicts to declare.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemphys.2019.02.015.

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