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Chemical Bonding in Novel 0-, 1-, 2-, and 3-Dimensional Chemical Species

Ivan A. Popov
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CHEMICAL BONDING IN NOVEL 0-, 1-, 2-, AND 3-DIMENSIONAL CHEMICAL SPECIES

by

Ivan A. Popov

A dissertation submitted in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY in Chemistry

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UTAH STATE UNIVERSITY Logan, Utah 2017
ABSTRACT

Chemical Bonding in Novel 0-, 1-, 2-, and 3-Dimensional Chemical Species

by

Ivan A. Popov, Doctor of Philosophy

Utah State University, 2017

Major Professor: Dr. Alexander I. Boldyrev
Department: Chemistry and Biochemistry

The work presented in this dissertation has been mainly focused on the investigation of chemical bonding in clusters observed in the photoelectron spectroscopy experiments or clusters isolated in the form of stable salts; hypervalent iodine molecules widely used in organic synthesis; various solid-state materials, which were either experimentally made or theoretically proposed. Using state-of-the-art theoretical tools, which were developed in the Boldyrev group, and designed for the chemical bonding analysis in molecular species (Adaptive Natural Density Partitioning method) and systems with periodic symmetry (Solid State Adaptive Natural Density Partitioning method) we analyzed geometric and electronic structures of the following species: Li₆Al₆H₂n+2 (n=2, 3), Li₂Al₃H₈⁻, and CoB₁₆⁻ atomic clusters; SₙF₄n+2 (n=2–9), SeₙF₄n+2 (n=2–9), IO₄⁻, PhIO, PhIO₂, PhIO₃, PhINR (R = SO₂Ph), and PhICR₂ (R = CO₂Me) molecules; [Au₂Sb₁₆]⁺ and [Ln(η⁴-Sb₄)₃]⁻ (Ln=La, Y, Ho, Er, Lu) solid phase clusters; -(SF₄–SF₄)ₓ⁻ and -(SeF₄–SeF₄)ₓ⁻ periodic chains; graphene, BC₃, and Cu₂Si atom-thin planar materials.
Based on the chemical bonding results obtained from the projects mentioned above, we concluded that a single Lewis structure is not sufficient for the correct description of electronic structure of the given system in most of these cases. On the contrary, introduction of multicenter (delocalized) bonding was shown to be absolutely crucial for understanding how atoms are bonded together. Essentially, the combination of intuitive simplicity of Lewis theory and generality of the canonical molecular orbital theory was found to be very effective for understanding why species adopt certain geometrical structures and what makes them stable. In this dissertation we have shown that the chemical bonding models developed on the basis of such findings could further be used for the rational design of novel clusters, molecules, and solid-state materials with tailored properties. Indeed, rational design of materials through understanding of their electronic structures is getting more credible and popular in chemistry and materials science. It is expected that the contribution to the development of chemical bonding made in this dissertation will help researchers design novel materials, which can be used in various areas of microelectronics, nanotechnology, and catalysis.

(314 pages)
Chemical Bonding in Novel 0-, 1-, 2-, and 3-Dimensional Chemical Species

Ivan A. Popov

While the trial and error approach is still being a dominant pathway for synthesis of various compounds in chemistry, computation-driven approaches have recently been shown to be a very efficient way towards the rational design of new materials with tailored properties. In principle, theoretical design of materials may not only significantly reduce the costs associated with the experiment, but may also result in the prediction of novel compounds possessing completely unexpected geometries. These compounds can serve as long-lived catalysts, powerful batteries, efficient solar cells, or reliable energy storage materials. Since geometric structure of any system is related to its electronic structure, it is very important to understand how atoms are bonded together since the chemical properties of materials depend upon the chemical bonds that make it up. Armed with this knowledge, researchers are able to develop theoretical models and design principles, which can be used to describe the geometry of the given system as well as rationally design novel species possessing desired structures and properties. The common thread of this dissertation was the development of the chemical bonding models for a vast range of chemical systems, including gas-phase clusters observed in a molecular beam or isolated in a condensed phase, various hypervalent iodine molecules, experimentally made two-dimensional materials of carbon and boron, as well as theoretically predicted molecular chains and atom-thin sheets awaiting their experimental confirmation.
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I would like to dedicate this dissertation to my loving parents: my father Alexander and my mother Tatyana for the beautiful life ticket they gave me. I am the happiest person in the world to have such caring parents who managed to go through all my study years together with me and helped me succeed in many endeavors.

Ivan A. Popov
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CHAPTER 1
INTRODUCTION

1-1. Chemical bonding theory tools

Undoubtedly, chemical bonding is one of the central concepts in chemistry, though not well-defined yet.\textsuperscript{1} For many years, scientists have been striving to develop a very general and rigorous concept, which could be powerful and useful, while still being chemically intuitive and simple to understand. Although many novel aspects of chemical bonding have already been discovered, the theory of chemical bonding keeps undergoing its rapid development. There is a huge number of various theories, concepts, techniques, and programs, which were designed for deciphering chemical bonding in clusters and molecules.\textsuperscript{2–36} They include but are not limited to the following: theory of molecular orbitals (MO) by Mulliken and Hund,\textsuperscript{2,3} different localization procedures proposed by Foster and Boys,\textsuperscript{4} Edmiston and Ruedenberg,\textsuperscript{5} Pipek and Mezey,\textsuperscript{6} valence bond theory coined by Heitler, London, Slater, and Pauling,\textsuperscript{7–9} quantum theory of atoms in molecules (QTAIM),\textsuperscript{10} local quantum-mechanical functions such as Fermi Hole (FH), electron localization function (ELF) and their various analogs.\textsuperscript{11–20} Chemical bonding analysis can also be done according to Coulson’s definition\textsuperscript{21} of bond order in polyatomic molecules, which was extended beyond the $\pi$-electron level by Wiberg.\textsuperscript{22} There are many other indices known, which allow users to assess bond orders. These examples include indices proposed by Mayer,\textsuperscript{23,24} Giambiagi,\textsuperscript{25} and Sannigrahi and Kar.\textsuperscript{26} Electron sharing indices such as Fulton’s electron sharing index (ESI),\textsuperscript{27,28} and delocalization indices (DI)\textsuperscript{29,30}
reviewed by Matito\textsuperscript{31} allow users to assess degree of electron delocalization and judge about the chemical bonding in a system.

One of the recent and very efficient tools capable of analyzing chemical bonding in clusters and molecules was developed in Prof. Boldyrev’s lab and is currently used in approximately 50 research groups around the world. It allows partitioning charge density in a chemically intuitive manner and is called the Adaptive Natural Density Partitioning (AdNDP) method.\textsuperscript{32} The algorithm is a generalization of the natural bonding orbital\textsuperscript{33,34} (NBO) analysis and is based on the diagonalization of the blocks of the first-order density matrix in the basis of natural atomic orbitals. AdNDP helps to express chemical bonding in terms of both localized and delocalized bonding elements. Localized elements of chemical bonding represent core electron pairs or valence electron pairs (one-center two-electron (1c-2e) objects) and classical two-center two-electron (2c-2e) bonds. They are also known as Lewis objects, in accordance with the most successful and generally accepted theory of chemical bonding, Lewis theory.\textsuperscript{35} When a single Lewis structure is not sufficient for a full description of the electronic structure of a system and multiple resonance Lewis structures are needed, delocalized (multicenter) bonding elements are evoked. This option ensures that the overall chemical bonding pattern is consistent with the symmetry of a system by providing single electronic structure, as opposed to the NBO method. Thus, AdNDP combines the compactness and intuitive simplicity of Lewis theory with the flexibility and generality of canonical MO theory.

Solid State Adaptive Natural Density Partitioning (SSAdNDP) is a recently developed tool\textsuperscript{36} designed to elucidate chemical bonding in systems with periodic symmetry, including infinitely long chains (1D), two-dimensional (2D) sheets, and three-
dimensional (3D) bulk materials. Similar to the molecular version (AdNDP), SSAdNDP can be used to interpret chemical bonding in terms of classical bonding elements (lone pairs and two-center bonds), as well as multicenter bonds. While there are other programs aimed at deciphering chemical bonding in periodic systems,4–6,37–43 they do not provide a localized, real space description that is commensurate with conventional Lewis theory. In contrast, recently developed Periodic NBO method44 constructs an optimal Lewis-like representation of bonding that allows obtaining localized elements. However, since the search for bonds is limited to two centers, it is necessary to include resonance structures to fully describe a system. This can be done by introducing the concept of multiple resonance structures via Natural Resonance Theory.45 It is important to note that such analysis can become cumbersome, especially when the number of potential resonance structures is high. SSAdNDP avoids resonance descriptions by identifying multicenter bonding motifs in addition to the Lewis structure elements, thus representing a very efficient and chemically intuitive tool that can be applicable to any kind of periodically extended systems.

1-2. 0-dimensional species: atomic clusters

In chemistry, atomic clusters (0D) are usually associated with ensembles of bound atoms that are intermediate in size between a molecule and a bulk solid.46 Hence, clusters may exhibit very specific properties, which are distinct from those of isolated molecules or bulk materials. Analysis of chemical bonding in such systems represents a fundamentally important avenue, which can be used to relate bonding with geometrical structure of a cluster, its stability, and reactivity. Essentially, understanding of how atoms
are bonded together is a very important step towards rational design of novel clusters, molecules, and solid-state materials, which can be used in nano-technology.

Atomic clusters can be observed in a molecular beam or under matrix isolation conditions. In the first technique, gas-phase clusters are produced in anion photoelectron spectroscopy (PES) experiments. PES is a powerful method to probe the electronic structure of species, providing necessary information about electronic states. Clusters are generated using laser vaporization and analyzed via a time-of-flight mass spectrometer. The cluster of interest is mass-selected and photodetached by a laser beam. The photoelectrons are analyzed in a magnetic-bottle photoelectron analyzer. In principle, PES spectrum serves as an “electronic fingerprint” of the cluster produced. Matrix isolation technique generally involves species being trapped within an unreactive matrix. A host matrix is a continuous solid phase, in which guest particles (atoms, clusters, ions) are embedded. A typical matrix isolation experiment involves a guest sample being diluted in the gas phase with the host material. Then, such mixture is deposited on a window that is cooled to below the melting point of the host gas.

In order to determine the structure of the produced cluster that usually corresponds to the global minimum (GM) energy structure on the potential energy surface due to the thermodynamic equilibrium achieved in the experiments, various GM search algorithms are employed. Subsequent accurate \textit{ab initio} calculations aid in establishing the most stable structure. In order to unequivocally verify that the GM structure established via the computational analysis is actually the one that is observed in the molecular beam, vertical electron detachment energies (VDEs) of the GM and lowest energy isomers are calculated and compared with the experimental VDEs. Once the GM
cluster is reliably established, its structure, stability, and electronic properties can be explained via chemical bonding analysis. Subsequently, chemical bonding models developed on the basis of such findings can further be used for the rational design of novel clusters with tailored properties.

Chapters 2-4 describe structures and chemical bonding of clusters, which were produced in molecular beam by two photoelectron spectroscopy groups: Prof. Wang from Brown University and Prof. Bowen from Johns Hopkins University. Geometrical structures of the clusters, which corresponded to the GM structures, were established by means of the Coalescence Kick method. The GM structures were checked to be contributors to the PES spectra by calculating VDEs and comparing their values with the experimental electron binding energies. Chemical bonding analyses were performed via NBO and AdNDP methods. Based on these results, novel clusters exhibiting very unique geometrical and electronic structures are proposed.

1-2.1. Aluminum-lithium-hydrogen mixed clusters

In contrast to the elements from Group 14, which are capable of forming rather long and stable homonuclear chains, Group 13 elements are rarely observed to form chain-like structures due to the favorable cluster formation. These examples include catenation of boron by a metal and catenation of borylene subunits without the use of strong alkali metals as reducing agents, LiB<sub>x</sub> species (with the approximate range 0.82<\(x\)<1.0) possessing chains of boron atoms surrounded by a lithium shell, Zintl-phase Cs<sub>10</sub>H[Ga<sub>3</sub>H<sub>8</sub>]<sub>3</sub> containing the propane-like polyanions [Ga<sub>3</sub>H<sub>8</sub>]<sup>3−</sup> and (K<sub>x</sub>Rb<sub>1-x</sub>)<sub>n</sub>[GaH<sub>2</sub>]<sub>n</sub> (<sub>x</sub>≤1) composed of [GaH<sub>2</sub>]<sup>n−</sup> anionic chains with a polyethylene
structure;\textsuperscript{71,72} indium containing chain-like species.\textsuperscript{73} Although a number of various Al-containing compounds have experimentally been observed before,\textsuperscript{74–76} formation of Al chain-like structures has remained illusive.

Chapter 2 reports a computational prediction of a new class of stable aluminum homocatenated Li\textsubscript{n}Al\textsubscript{n}H\textsubscript{2n+2} compounds\textsuperscript{77} based on the electronic transmutation concept proposed by Olson and Boldyrev.\textsuperscript{78} Chemical bonding analyses of Li\textsubscript{2}Al\textsubscript{2}H\textsubscript{6} and Li\textsubscript{3}Al\textsubscript{3}H\textsubscript{8} clusters have shown a presence of direct Al–Al σ bonds, constituting kernels of these chain-like species. Chapter 3 confirms the computational predictions made for the Li\textsubscript{3}Al\textsubscript{3}H\textsubscript{8} cluster on the example of the isoelectronic Li\textsubscript{2}Al\textsubscript{3}H\textsubscript{8}– cluster, which was experimentally observed in molecular beam experiments.\textsuperscript{79}

I-2.2. Transition metal-centered boron sub-nano “drums”

Due to the electron-deficient nature of boron and its strong bonding capacity,\textsuperscript{80,81} a vast variety of various pure and doped boron clusters has been theoretically predicted and experimentally observed in molecular beam during the last 17 years.\textsuperscript{67,82} Structures common for bulk boron\textsuperscript{83–85} were shown to be quite different from the ones found in molecular beam. In fact, anionic boron clusters have been found to exhibit planar or quasi-planar structures in their ground states up to 36 atoms.\textsuperscript{86–91} Recent discoveries of the remarkable fullerene-like structures of B\textsubscript{40}– and B\textsubscript{39}– clusters\textsuperscript{92,93} have further enriched the diversity of boron sub-nano clusters, thus introducing a 2D-to-3D structural transition.

Formation of boron clusters possessing unusual geometries and chemical bonding patterns has been shown to be possible via doping with a single transition metal atom. Using this approach, various molecular wheel-type structures (M@B\textsubscript{20})\textsuperscript{94} of boron were
theoretically proposed and experimentally realized following an electronic design principle inspired by the doubly $\sigma$ and $\pi$ aromatic $B_9^-$ cluster.\textsuperscript{95} Two such clusters (Nb@B$_{10}^-$ and Ta@B$_{10}^-$) were found to possess the highest coordination number of 10 in the planar environment for the central metal atom.\textsuperscript{96}

It was further shown that doping of pure boron clusters with a transition metal atom could induce an earlier 2D-to-3D structural transition in the series of anionic boron clusters.\textsuperscript{97,98} Chapter 4 reports a joint photoelectron spectroscopy and theoretical study of the CoB$_{16}^-$ cluster,\textsuperscript{97} which was found to exhibit a highly symmetric 3D tubular structure reminiscent of a drum. It is worthy to note that understanding of its electronic structure aided in the design of novel drum-like boron clusters, such as MnB$_{16}^-$,\textsuperscript{98} RhB$_{18}^-$,\textsuperscript{99} and TaB$_{20}^-$\textsuperscript{100}

1-3. 1-dimensional species: extended nonmetal atom chains

At the beginning of the century, Cotton and co-workers introduced a concept of extended metal atom chain (EMAC) complexes.\textsuperscript{101} Such compounds refer to the chain-like species made out of metals atoms, which are surrounded by various stabilizing groups. As a matter of fact, the first compound containing three Ni atoms in a chain-like fashion was reported well before that in 1968.\textsuperscript{102} Since then, many other EMAC species were discovered.\textsuperscript{103–108} Molecular compounds containing linear chains of nonmetal atoms are also known, but their number is smaller.\textsuperscript{109–111}

Chapter 5 investigates a viability of the extended nonmetal atom chains (ENAC) based on molecular models with the general formula $M_n F_{4n+2}$ ($M=\text{S and Se}$) and corresponding solid-state systems exhibiting direct either S–S or Se–Se bonding in a
chain-like fashion.\textsuperscript{112} Chemical bonding analyses of the molecular compounds and periodically extended chains were performed via AdNDP and SSAdNDP methods, respectively.

\textbf{1-4. 2-dimensional species: atomic-thin sheets}

Since the isolation of graphene and discovery of its unusual properties,\textsuperscript{113} myriads of novel 2D materials have been theoretically predicted, and many of them have been experimentally realized afterwards. Reduced dimensionality provides us with a great opportunity to explore unique monolayer systems exhibiting unusual geometries, fascinating properties, and unexpected chemical bonding patterns. Chapters 6-8 describe results of the chemical bonding analyses obtained for graphene,\textsuperscript{114} BC\textsubscript{3} honeycomb epitaxial sheet,\textsuperscript{115} and newly predicted Cu\textsubscript{2}Si monolayer.\textsuperscript{116}

\textit{1-4.1. Graphene}

Understanding of chemical bonding in the ideal graphene system is fundamentally important task as it may help explain chemical bonding in more complicated cases, where the framework of the symmetrically distributed sp\textsuperscript{2} hybridized carbon atoms forming a honeycomb structure is somewhat modified. That refers to point defects, single-, double- and multiple vacancies, carbon adatoms, foreign adatoms, and substitutional impurities.\textsuperscript{117} We believe that the chemical bonding pattern obtained for graphene may further be used to explain bonding interactions in new materials that are derivatives of graphene. Chapter 6 reveals results of the chemical bonding analysis of graphene that sheds light on its aromatic character.\textsuperscript{114}
1-4.2. *Boron-carbon sheets of various stoichiometry*

Inspired by the remarkable example of honeycomb structure composed of carbon atoms, various pure boron\textsuperscript{118,119} and mixed boron-carbon\textsuperscript{120,121} 2D sheets have been proposed and intensively investigated. Interestingly, most of the global minimum structures of different boron-carbon monolayers have been shown to be metallic, whereas highly symmetric BC\textsubscript{3} sheet appeared to be a “magic case” showing a semi-conducting behavior.\textsuperscript{121} To the best of our knowledge, BC\textsubscript{3} sheet is the only one experimentally produced boron-carbon 2D system, the structure of which was determined by low-energy electron diffraction.\textsuperscript{120} Chapter 7 explains the structure and stability of this unique monolayer via the AdNDP analysis that revealed the so-called “islands of stability” over all hexagons composed of carbon atoms.

1-4.3. *Planar hyper-coordinate sheets*

Due to the difficulty in stabilizing planar hypercoordinated configurations in extended systems, 2D materials with planar hypercoordinate motifs are very rare. The experimental examples include nickel carbide polymer network Ca\textsubscript{4}Ni\textsubscript{3}C\textsubscript{5} featuring planar tetracoordinate carbon atoms.\textsuperscript{122} Theoretically predicted systems include hexagonal close-packed monolayers of silver\textsuperscript{123} and gold,\textsuperscript{124} various hyper-coordinated boron sheets.\textsuperscript{119,125–127} However, taking into account pretty fast development of experimental techniques for fabrication of novel 2D systems recently, scientists are optimistic that such materials will be synthesized, either as freestanding layers or on a substrate. We believe that unusual coordination and reduced dimensionality can result in the rule-breaking chemical bonding patterns that can lead to the realization of completely
new materials, which are of fundamental importance to chemistry and materials science. Chapter 8 reports a theoretical study on novel hypercoordinate material Cu$_2$Si, where each Si atom is coordinated to six Cu atoms, and each Cu atom is coordinated to three Cu and three Si atoms. SSAdNDP analysis has shown that only multicenter bonding elements govern completely planar geometry of this one-atom thin material.\textsuperscript{116}

1-5. 3-dimensional species: solid phase materials

Development of novel advanced techniques for chemical bonding analyses allows one to get accurate results in electronic structure calculations, which sometimes may provide us with completely unexpected results. Chapter 9 reports a computational study\textsuperscript{128} on series of hypervalent iodine compounds, which are widely used in organic synthesis.\textsuperscript{129} Results of the AdNDP analyses obtained for these species show that the chemical bonding notation that has been used for many years appears to be qualitatively wrong, and suggests the textbooks may need correcting.

As opposed to Chapters 2-4, where we analyze chemical bonding in gas-phase clusters, Chapters 10 and 11 describe joint experimental and computational studies of novel clusters, which were isolated in condensed phase and identified by single-crystal X-ray diffraction.\textsuperscript{130,131} The studies expand many rules designed for short-lived clusters found in molecular beam experiments towards the condensed phase.

1-5.1. Hypervalent iodine compounds

Hypervalent iodine compounds represent an interesting class of organic molecules, which have found wide application as versatile, efficient, and environmentally sustainable reagents.\textsuperscript{129} X-ray structural studies of these compounds in the solid state are
inconclusive because the real molecular structure of hypervalent iodine derivatives is masked by extensive networks of intermolecular secondary bonds resulting in a highly aggregated polymeric structure.\textsuperscript{132,133} Chapter 9 reports results of the AdNDP analysis for various hypervalent iodine molecules that firmly establish the nature of chemical bonding between iodine and oxygen, iodine and nitrogen, and iodine and carbon.\textsuperscript{128}

1-5.2. \textit{All-metal aromatic and antiaromatic clusters}

The synthesis of solid-state compounds with antiaromatic building blocks is unquestionably very challenging because of their low stability and high reactivity. According to Breslow,\textsuperscript{134,135} antiaromaticity usually refers to monocyclic systems with $4n\pi$ electrons. For the first time, this concept was extended to all-metal molecules after the observation of Li$_3$Al$_4^-$ in the gas phase.\textsuperscript{136} However, $\pi$ antiaromatic solid-phase counterparts have not been reported thus far. Chapter 10 describes a series of all-metal antiaromatic anions, [Ln($\eta^4$-Sb$_4$)$_3$]$^{3-}$ (Ln=La, Y, Ho, Er, Lu), which were made in condensed phase.\textsuperscript{130} Chapter 11 shows another example of a very unique solid state cluster anion [Au$_2$Sb$_{16}$]$^{4-}$, which possesses the largest unfragmented Sb$_n$ polyanion isolated from solution\textsuperscript{131} that is possible due to the aromatic character of the cluster.

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CHAPTER 2

HOMOCATENATION OF ALUMINUM: ALKANE-LIKE STRUCTURES OF
Li$_2$Al$_2$H$_6$ and Li$_3$Al$_3$H$_8$$^1$

Abstract

A new class of aluminum homocatenated compounds (Li$_n$Al$_n$H$_{2n+2}$) is proposed based on quantum chemical calculations. In these compounds, Al abstracts an electron from Li, becoming valence isoelectronic with C, Si, and Ge, thus mimicking respective structural features of Group 14 hydrides. Using the Coalescence Kick search program coupled with density functional theory calculations, we investigated the potential energy surfaces of Li$_2$Al$_2$H$_6$ and Li$_3$Al$_3$H$_8$. Then single-point-energy coupled-cluster calculations were performed for the lowest energy structures found. Indeed, the global minima established for Li$_2$Al$_2$H$_6$ and Li$_3$Al$_3$H$_8$ contain the Al$_2$H$_6^{2-}$ and Al$_3$H$_8^{3-}$ kernels, which are isostructural with ethane (C$_2$H$_6$), disilane (Si$_2$H$_6$), digermane (Ge$_2$H$_6$) and propane (C$_3$H$_8$), trisilane (Si$_3$H$_8$), trigermane (Ge$_3$H$_8$) molecules, respectively. Structural, energetic, and electronic characteristics of the Li$_2$Al$_2$H$_6$ and Li$_3$Al$_3$H$_8$ compounds are presented and the viability of their synthesis is discussed.

The capacity of an atom to form classical single bonds with itself producing chain-like structures is strongly dependent on its nature and environment. The so-called atomic catenation of carbon has certainly played an important role in the life formation,$^{[1]}$ which is reflected by the vast range of zigzag-chained C$_n$H$_{n+2}$ alkanes. Homocatenation

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of silicon is also well known though the increasing decomposition reaction rate, which increases with the number of silicon atoms, makes preparation and isolation of \( \text{Si}_{n}\text{H}_{2n+2} \) silanes with \( n>8 \) difficult.\[2\] Homocatenated species of heavier congeners from Group 14 become increasingly scarce as the atomic weight increases, since more diffuse valence orbitals and higher inner shell repulsion increases the tendency of homolytic decomposition of long chains.\[3\] In contrast to carbon and silicon, Group 13 elements are very rarely observed to catenate into linear chains. Although boron may form strong B–B bonds, its favorable cluster formation\[4\] makes homocatenation very difficult. The first observation of both catenation of boron by a metal and catenation of borylene subunits without the use of strong alkali metals as reducing agents has been recently made by Braunschweig et al.\[5\] This unique discovery shows great promise for the controlled construction of one-dimensional boron chains. One more rare experimental example for this group is a linear homocatenated compound containing six indium centers that was produced by the treatment of indium(I) iodide with a protonated \( N \)-xylyl \( \beta \)-diketiminate and a strong potassium base in tetrahydrofuran.\[6\]

Another avenue for homocatenation is the use of the isoelectronic principle, which may help in designing materials that are isoelectronic to known compounds. Very recently, Fahlquist et al. have demonstrated the viability of this rule on couple of examples: a remarkable hydrogenous Zintl-phase \( \text{Cs}_{10}\text{H}[\text{Ga}_{3}\text{H}_{8}]_{3} \) containing the propane-like polyanions \([\text{Ga}_{3}\text{H}_{8}]^{-} \)[7] and \((\text{K}_{x}\text{Rb}_{1-x})_{n}[\text{GaH}_{2}]_{n} (0 \leq x \leq 1)\) composed of \([\text{GaH}_{2}]^{-n} \) anionic chains with a polyethylene structure.\[8\] The same principle was applied more than decade ago by Wörle and Nesper, who demonstrated the existence of pure-phase \( \text{LiB}_{x} \) samples (with the approximate range \( 0.82<x<1.0 \)) possessing a chain of boron atoms
surrounded by a lithium shell that illustrates the structural analogy between borynide chains in LiB₃ and isoelectronic polyynes and polycumulene chains.\textsuperscript{[9]}

A more narrowed definition of the isoelectronic principle, the so-called electronic transmutation concept, which was used in many theoretical predictions, was introduced by Olson and Boldyrev.\textsuperscript{[10]} It has been shown that boron acquiring an extra electron in borohydrides forms molecular analogues of homocatenated saturated hydrocarbons.\textsuperscript{[10]} Earlier, the isoelectronic equivalence of carbon by B\textsuperscript{−} has been shown for many species by Jemmis and Jayasree\textsuperscript{[11a]} and Alexandrova et al.\textsuperscript{[11b]} Osorio et al. have explored a variety of boron homocatenated compounds in the BₙH\textsubscript{n+2} series,\textsuperscript{[12]} which is supposed to be analogous to those of CₙH\textsubscript{2n+2}. Very recently, it was shown by Poater et al. that classical organic polycyclic aromatic hydrocarbons (PAH) and closo-borohydride clusters share a common origin regulated by the number of valence electrons in an electronic confined space.\textsuperscript{[13]} Different cases of boron homocatenated compounds stabilized by lithium and hydrogen atoms were theoretically tested.\textsuperscript{[14]} A number of theoretical studies on different compounds mimicking common organic species is reported elsewhere.\textsuperscript{[15]} Theoretical and experimental evidences of other main-group homocatenated compounds are also known.\textsuperscript{[16]}

Exceptional experimental results of homocatenation known for boron, gallium, and indium suggest aluminum may also form similar compounds; though we are not aware of such reports. In this communication we investigate the viability of aluminum homocatenated compounds based on the concept of electronic transmutation and their similarity to corresponding alkane analogues, which are isostructural with their respective silanes and germanes. Similar to the experimentally observed Cs\textsubscript{10}H[Ga\textsubscript{3}H\textsubscript{8}]\textsubscript{3} with
[Ga$_3$H$_8$]$^{3-}$ polyanions possessing a propane-like kernel,[7] we have combined lithium, hydrogen, and aluminum atoms to design alkane-like structures of the general formula Li$_n$Al$_n$H$_{2n+2}$ for $n=2$ and 3.

Due to the huge number of different geometrical configurations arising from the combination of three types of atoms with the total number of atoms equal to ten (Li$_2$Al$_2$H$_6$) and 14 (Li$_3$Al$_3$H$_8$), the potential energy surface (PES) for both stoichiometric compositions is inherently complicated, thus representing a myriad of structures. Therefore, to make our search reliable, a large population (thirty thousand trial structures) was generated for each species by using the Coalescence Kick (CK) program[17] written by Averkiev to follow the geometry optimization procedure with the Gaussian 09 program.[18] The exhaustive search results were sorted out for the lowest energy isomers within 30 and 25 kcal mol$^{-1}$ at the PBE0[19]/LanL2DZ[20] level of theory for Li$_2$Al$_2$H$_6$ and Li$_3$Al$_3$H$_8$, respectively. These low-lying isomers were refined by using the more expansive 6-311++G(d, p) basis set[21] for PBE0 (geometry optimization and follow-up frequency analyses to ensure that each structure is a minimum on the PES) and CCSD(T) (single-point calculations) methods to give more accurate relative energies. CCSD(T)/6-311++G(d, p)//PBE0/6-311++G(d, p) results are shown in parentheses in Figure 2-1.

It turned out that the baffling complexity of the PES revealed for both isomers is aggravated by its mildly sloping nature. In fact, 23 isomers of Li$_2$Al$_2$H$_6$ and 77 isomers of Li$_3$Al$_3$H$_8$ were found within 20 kcal mol$^{-1}$ at the DFT level (Figures 2-2 and 2-3). The global minimum (GM) structure of Li$_2$Al$_2$H$_6$ (Figure 2-1) was found to possess a geometry resembling that of an eclipsed ethane conformer, straying from the traditional staggered conformation. Favoring the eclipsed conformation is likely due to an increased
Al–Al bond length in I.1 relative to the C–C bond in ethane: $R(\text{Al–Al})=2.69$ Å versus $R(\text{C–C})=1.52$ Å. On the one hand, this change causes a weakening of hyperconjugation, which plays a very important role in stabilization, as shown by several studies on ethane,\textsuperscript{[22]} though some studies\textsuperscript{[23]} emphasize the importance of steric effects. On the other hand, such an arrangement favors more effective interaction with the lithium atoms. In fact, four hydrogen atoms in I.1 are almost coplanar with two lithium atoms and well centered, which helps enhance the interaction. As a result of the lithium–hydrogen interaction, four Al–H bonds are substantially longer than two others (1.70 vs. 1.60 Å) and the corresponding Al–Al–H angle is significantly smaller (101.1° vs. 131.7°).

In contrast, the GM structure of its boron analogue\textsuperscript{[10]} Li$_2$B$_2$H$_6$ adopts a staggered conformation of the B$_2$H$_6^{2-}$ kernel due to the increased hyperconjugation arising from the shorter bond length ($R(\text{B–B})=1.81$ Å).\textsuperscript{[10]} Interestingly, similar to alkanes, conformational isomers were also observed for our "aluminum homocatenated ethane". The closest in energy isomers I.2 and I.3 are 0.9 and 6.6 kcal mol$^{-1}$ higher in energy, respectively, at CCSD(T) level and represent staggered conformations of the Al$_2$H$_6^{2-}$ kernel with different arrangement of lithium atoms, that is apparently less effective than in I.1.

The unbiased CK search for Li$_3$Al$_3$H$_8$ yielded a propane-like kernel resembling the predicted analogue\textsuperscript{[10]} for Li$_3$B$_3$H$_8$ and the experimentally observed kernel from Cs$_{10}$H[Ga$_3$H$_8$].\textsuperscript{[7]} However, there are some deviations from the perfect propane-like geometry in the "aluminum homocatenated propane". As seen from Figure 2-1, isomer II.1 possesses $C_s$ point-group symmetry with the center carbon tilting the two hydrogen atoms towards the lithium atoms and away from another symmetrical plane. Furthermore,
while the C–C–C valence angle in propane (112.8°) differs slightly from the respective one in Li₃B₃H₈ (116.0°), it is substantially reduced to 92.5° in Li₃Al₃H₈ (Table 2-1). Similar to Li₂Al₂H₆, one can see the pronounced effect of lithium–hydrogen interaction. Apparently, due to aluminum’s larger radii and, therefore, weakened stabilization relative to C₃H₈ and B₃H₈³⁻, the charge interactions take control of the geometric stability in Li₃Al₃H₈. Interestingly, the largest angle formed by the Group 13 elements in the homocatenated species is observed in [Ga₃H₈]³⁻ polyanions⁷ (Table 2-1), which is in agreement with the significantly larger atomic radii of cesium metal stabilizing the gallium chain. Despite slight structural discrepancies in the propane-like kernel, the bond lengths in Li₃Al₃H₈ are very similar to those of Li₂Al₂H₆: \( R(Al-Al) = 2.67 \) Å, \( R(Al-H) = 1.59-1.60 \) Å for three hydrogen atoms that are not interacting with lithium atoms and \( R(Al-H) = 1.67-1.74 \) Å for the other five hydrogen atoms located closer to the lithium atoms. The five lowest energy structures are noteworthy as they maintain the propane-like kernel before other geometric structural possibilities are introduced (Figure 2-3). Furthermore, isomer II.3 looks the same as the GM structure of Li₃B₃H₈, but the increased Al–Al bond length relative to that of B–B, coupled with less effective arrangement of lithium atoms in II.3, makes this isomer less stable than II.1.

Essentially, the evident structural analogy with their respective alkanes found for the first two members of the LiₙAlₙH₂ₙ₊₂ family should coincide with their electronic structures. In order to check this, we have performed chemical bonding analyses by using the natural bond orbital (NBO) method²⁴ at the PBE0/6-311++G(d, p) level of theory. Chemcraft 1.6²⁵ and Molekel 5.4.0.8²⁶ programs were used for structural and molecular orbitals visualization (Figure 2-4).
Undoubtedly, the homocatenation has taken place in both species: NBO has revealed classical two-center two-electron (2c-2e) Al−Al σ bonds with an occupation number (ON)=1.9 |e|, which is very close to the ideal value of 2.0 |e|. Additionally, the analyses indicate six and eight Al−H σ bonds with ON=1.9−2.0 |e| for Li₂Al₂H₆ and Li₃Al₃H₈ compounds, respectively. Al−H σ bonding is highly polarized towards hydrogen (around 24−37% of electron density comes from aluminum). Comparative pictures of chemical bonding obtained for corresponding alkane molecules are shown in Figure 2-5. Striking similarities are evident: all the bonds are analogous, with similar ON values. Natural population analysis (NPA) charges (Tables 2-2 and 2-3) confirm that both aluminum-containing compounds have acquired one electron from each lithium atom and electronically transmuted into their carbon analogues: \( q(\text{Li})=+0.89 \), \( q(\text{Al}_2\text{H}_6 \ \text{fragment})=-1.77 \) in I.1 and \( q(\text{Li})=+0.86 \), \( q(\text{Al}_3\text{H}_8 \ \text{fragment})=-2.60 \) in I.1. Interestingly, rotational conformers I.2 and I.3 were found to have very similar NPA charges (Table 2-2). Probably, it enabled adopting the ethane-like geometry of staggered conformation possessing the same number of bonds with similar ON values (Table 2-4), though the arrangement of lithium cations in I.1 favors the eclipsed geometry. Similarly, the charge interactions take control over the geometric stability in Li₃Al₃H₈: five isomers II.1–II.5 with very similar propane-like kernels have quite similar NPA charges on lithium atoms and the same bonds with ONs close in value (Tables 2-3 and 2-5). However, isomer II.1 with the shortest Al−Al−Al angle due to the particular arrangement of the lithium atoms is found as the GM. Notably, relative to other isomers with similar AlₙH₂ₙ₊₂ kernels, the GM structures of both species contain the highest number of unperturbed Al−H σ bonds, thus maintaining the structural features of alkanes. This is reflected in the ON values of
these bonds (which are higher than the lithium-affected ones) and charges on hydrogen atoms (which are less negative than on the perturbed ones) (Tables 2-2-2-5). These observations are in excellent agreement with the Al–H bond lengths: the shorter the bond, the weaker the lithium–hydrogen interaction. Evidently, because of that the structural features of the ethane- and propane-like kernels are more preserved in I.1 and II.1, respectively, which probably makes them more favorable relative to other similar isomers.

In summary, the current work has firmly established a new class of stable aluminum homocatenated LiₙAlₙH₂ₙ₊₂ compounds. For the first time it has been shown the electronic transmutation enables aluminum atoms to homocatenate with the formation of alkane-like species. Chemical bonding analyses of Li₂Al₂H₆ and Li₃Al₃H₈ have confirmed striking similarities of the aluminum–hydrogen kernel with their respective alkanes. Due to the significant progress on fabrication of similar materials made in recent years, we are hopeful that these species or their analogs can also be made experimentally in the near future. We believe these alkane-like clusters in aluminum hydride materials have significant implications for the discovery of hydrides for hydrogen storage as well as new reducing agents.

References


[26] U. Varetto, Molekel 5.4.0.8, Swiss National Supercomputing Centre: Manno, Switzerland, 2009.
Tables and Figures

Table 2-1. X-X-X valence angle values (deg.) of propane and X-homocatenated propane-like species (X=B, Al, Ga) for C₃H₈, Li₃B₃H₈, Li₃Al₃H₈, and Cs₁₀H[Ga₃H₈]₃.

<table>
<thead>
<tr>
<th></th>
<th>C₃H₈ᵃ</th>
<th>Li₃B₃H₈ᵃ</th>
<th>Li₃Al₃H₈ᵇ</th>
<th>Cs₁₀H[Ga₃H₈]₃ᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>112.8</td>
<td>116.0</td>
<td>92.5</td>
<td>120.1</td>
</tr>
</tbody>
</table>

ᵃ Calculated at the PBE0/6-311++G(d, p) levels of theory.
ᵇ From ref. 7.

Table 2-2. NPA charges on atoms in I.1-I.3 isomers of Li₂Al₂H₆ at the PBE0/6-311++G(d, p) level of theory. Hydrogen atom charges indicated in bold are free of lithium atom interactions here and elsewhere.

<table>
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<tr>
<th>Atoms</th>
<th>I.1</th>
<th>I.2</th>
<th>I.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li₁</td>
<td>0.88712</td>
<td>0.86669</td>
<td>0.88545</td>
</tr>
<tr>
<td>Li₂</td>
<td>0.88712</td>
<td>0.86669</td>
<td>0.92016</td>
</tr>
<tr>
<td>Al₃</td>
<td>0.24008</td>
<td>0.31869</td>
<td>0.20996</td>
</tr>
<tr>
<td>Al₄</td>
<td>0.24008</td>
<td>0.31869</td>
<td>0.36817</td>
</tr>
<tr>
<td>H₅</td>
<td>-0.42151</td>
<td>-0.49041</td>
<td>-0.40240</td>
</tr>
<tr>
<td>H₆</td>
<td>-0.28417</td>
<td>-0.40324</td>
<td>-0.40240</td>
</tr>
<tr>
<td>H₇</td>
<td>-0.28417</td>
<td>-0.49041</td>
<td>-0.28444</td>
</tr>
<tr>
<td>H₈</td>
<td>-0.42151</td>
<td>-0.29173</td>
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</tr>
<tr>
<td>H₉</td>
<td>-0.42151</td>
<td>-0.40324</td>
<td>-0.39560</td>
</tr>
<tr>
<td>H₁₀</td>
<td>-0.42151</td>
<td>-0.29173</td>
<td>-0.50330</td>
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Table 2-3. NPA charges on atoms in II.1-II.5 isomers of Li$_3$Al$_3$H$_8$ at the PBE0/6-311++G(d, p) level of theory.

<table>
<thead>
<tr>
<th>Atoms</th>
<th>II.1</th>
<th>II.2</th>
<th>II.3</th>
<th>II.4</th>
<th>II.5</th>
</tr>
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<tbody>
<tr>
<td>Li$_1$</td>
<td>0.88332</td>
<td>0.90479</td>
<td>0.86208</td>
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<td>Li$_2$</td>
<td>0.85379</td>
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<td>0.85362</td>
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<tr>
<td>Li$_3$</td>
<td>0.86217</td>
<td>0.86541</td>
<td>0.89896</td>
<td>0.86671</td>
<td>0.89829</td>
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<tr>
<td>Al$_4$</td>
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<td>0.14476</td>
<td>0.32966</td>
<td>0.41017</td>
<td>0.43306</td>
</tr>
<tr>
<td>Al$_5$</td>
<td>0.25662</td>
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<td>0.32966</td>
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<td>0.18990</td>
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<tr>
<td>Al$_6$</td>
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<td>H$_7$</td>
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<td>-0.40821</td>
<td>-0.44338</td>
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<tr>
<td>H$_8$</td>
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<td>-0.43085</td>
<td>-0.37273</td>
<td>-0.41058</td>
<td><strong>-0.28283</strong></td>
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<tr>
<td>H$_9$</td>
<td><strong>-0.28189</strong></td>
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<td>-0.37273</td>
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<td>H$_{10}$</td>
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<td>-0.32509</td>
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<td>H$_{11}$</td>
<td>-0.46831</td>
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<td>-0.41821</td>
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<td><strong>-0.28954</strong></td>
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<tr>
<td>H$_{12}$</td>
<td><strong>-0.26035</strong></td>
<td>-0.36872</td>
<td>-0.40305</td>
<td>-0.42025</td>
<td>-0.39609</td>
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<tr>
<td>H$_{13}$</td>
<td><strong>-0.28189</strong></td>
<td>-0.33594</td>
<td>-0.40305</td>
<td><strong>-0.29182</strong></td>
<td>-0.48419</td>
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<td>H$_{14}$</td>
<td>-0.45814</td>
<td><strong>-0.29315</strong></td>
<td><strong>-0.28808</strong></td>
<td><strong>-0.29182</strong></td>
<td>-0.37476</td>
</tr>
</tbody>
</table>
Table 2-4. ON values of bonds and their averaged values found by the NBO analyses for I.1-I.3 isomers of Li$_2$Al$_2$H$_6$ at the PBE0/6-311++G(d, p) level of theory.

| Isomers | ON(Al-Al), |e| | ON(Al-H), |e| |
|---------|------------|----|----------------|-----|
| I.1     | 1.92       |    | (1.93+1.99+1.93+1.99+1.93+1.93)/6=1.95 |
| I.2     | 1.92       |    | (1.89+1.93+1.99+1.93+1.89+1.99)/6=1.94 |
| I.3     | 1.96       |    | (1.95+1.95+1.99+1.93+1.93+1.93)/6=1.95 |

Table 2-5. ON values of bonds and their averaged values found by the NBO analyses for II.1-II.5 isomers of Li$_3$Al$_3$H$_8$ at the PBE0/6-311++G(d, p) level of theory.

| Isomers | ON(Al-Al), |e| | ON(Al-H), |e| |
|---------|------------|----|----------------|-----|
| II.1    | (1.90+1.90)/2=1.90 |    | (1.91+1.99+1.91+1.91+1.99+1.91+1.99+1.91)/8=1.94 |
| II.2    | (1.91+1.96)/2=1.94 |    | (1.95+1.95+1.94+1.90+1.95+1.93+1.91+1.99)/8=1.94 |
| II.3    | (1.93+1.93)/2=1.93 |    | (1.93+1.93+1.99+1.93+1.99+1.93+1.94+1.94/8=1.95 |
| II.4    | (1.93+1.93)/2=1.93 |    | (1.92+1.93+1.99+1.92+1.88+1.92+1.93+1.99)/8=1.94 |
| II.5    | (1.96+1.92)/2=1.94 |    | (1.89+1.99+1.91+1.91+1.99+1.94+1.95+1.88)/8=1.94 |
Figure 2-1. The ground electronic states, point-group symmetries, and relative energies of the five lowest lying isomers of Li$_2$Al$_2$H$_6$ (top) and Li$_3$Al$_3$H$_8$ (bottom) at PBE0 and CCSD(T) levels of theory. Color scheme: blue is hydrogen; yellow is aluminum; magenta is lithium. All energies are in kcal mol$^{-1}$. 
Figure 2-2. Optimized isomers of Li$_2$AlH$_6$, their point group symmetries, spectroscopic states, and ZPE corrected relative energies at the PBE0/6-311++G(d, p) and CCSD(T)/6-311++G(d, p)//PBE0/6-311++G(d, p) (in parentheses) levels of theory. The solid rods between atoms help visualization and do not necessarily represent 2c-2e bonds here and elsewhere.
Figure 2.3. Optimized isomers of Li₃Al₃H₈, their point group symmetries, spectroscopic states and ZPE corrected relative energies at the PBE0/6-311++G(d, p) and CCSD(T)/6-311++G(d, p)//PBE0/6-311++G(d, p) (in parentheses) levels of theory. ZPE corrections for single-point coupled-cluster calculations were made with the PBE0 zero-point energies here and elsewhere.
Figure 2-3 Continued
Figure 2-4. NBO results for a) Li_2Al_2H_6: one 2c-2e Al–Al σ bond (left) and six 2c-2e Al–H σ bonds (right, shown superimposed) and b) for Li_3Al_3H_8: two 2c-2e Al–Al σ bonds (left, shown superimposed) and eight 2c-2e Al–H σ bonds (right, shown superimposed). ON denotes occupation number.

Figure 2-5. The ground electronic states, point group symmetries and NBO results a) for ethane: one 2c-2e C–C σ bond (center) and six 2c-2e C–H σ bonds (right, shown superimposed) and b) for propane: two 2c-2e C–C σ bonds (center, shown superimposed) and eight 2c-2e C–H σ bonds (right, shown superimposed).
CHAPTER 3
ALUMINUM CHAIN IN Li$_2$Al$_3$H$_8$\textsuperscript{−} AS SUGGESTED BY PHOTOELECTRON SPECTROSCOPY AND AB INITIO CALCULATIONS\textsuperscript{1}

Abstract

Group 13 elements are very rarely observed to catenate into linear chains and experimental observation of such species is challenging. Herein we report unique results obtained via combined photoelectron spectroscopy and ab initio studies of the Li$_2$Al$_3$H$_8$\textsuperscript{−} cluster that confirm the formation of an Al chain surrounded by hydrogen atoms in a very particular manner. Comprehensive searches for the most stable structure of the Li$_2$Al$_3$H$_8$\textsuperscript{−} cluster have shown that the global minimum isomer I possesses a geometric structure, which resembles the structure of propane, similar to the experimentally known Zintl-phase Cs$_{10}$H[Ga$_3$H$_8$]$_3$ compound featuring the propane-like [Ga$_3$H$_8$]$^{3−}$ polyanions. Theoretical simulations of the photoelectron spectrum have demonstrated the presence of only one isomer (isomer I) in the molecular beam. Chemical bonding analysis of the Li$_2$Al$_3$H$_8$\textsuperscript{−} cluster has revealed two classical Al–Al σ bonds constituting the propane-like kernel.

3-1. Introduction

Scarce examples of compounds featuring Group 13 metal–metal (M–M) single bonds represent unique cases deserving much attention. The chance for the experimental

\textsuperscript{1} Coauthored by Ivan A. Popov, Xinxing Zhang, Bryan W. Eichhorn, Alexander I. Boldyrev and Kit H. Bowen. Reproduced from Phys. Chem. Chem. Phys. 2015, 17, 26079–26083 with permission from the PCCP Owner Societies.
verification of the extended species featuring M–M bonding in a chain-like fashion is even smaller and hence fundamentally important. In contrast to Group 14 elements, which are quite frequently observed to form long and stable homonuclear chains,\(^1\) Group 13 elements tend to form cluster-like species instead.\(^2\) Homocatenated boron chains and rings of up to only eight boron atoms are known up to date.\(^3\) Catenation of boron by a metal and catenation of borylene subunits without the use of strong alkali metals as reducing agents has been recently made by Braunschweig \textit{et al.} thus representing a unique example known for boron.\(^4\) Recent efforts to provide new, mild, functional-group-tolerant, and convenient synthetic methods for the formation of electron-precise B–B single bonds have been summarized elsewhere.\(^5\) The use of the electronic transmutation principle\(^6\) and similar Zintl–Klemm concept\(^7\) have enabled designing novel materials, which are isoelectronic and isostructural to existing compounds. Wörle and Nesper demonstrated the existence of pure-phase LiB\(_x\) samples (with the approximate range 0.82 \(< x < 1.0\)) possessing chains of boron atoms surrounded by a lithium shell that illustrate the structural analogy between boryni de chains in LiB\(_x\) and isoelectronic polyyne and polycumulene chains.\(^8\) Fahlquist \textit{et al.} have shown the viability of this concept for gallium containing species: a hydrogenous Zintl-phase Cs\(_{10}\)H[Ga\(_3\)H\(_8\)]\(_3\) featuring the propane-like polyanions\(^9\) [Ga\(_3\)H\(_8\)]\(^-\) and (K\(_x\)Rb\(_{1-x}\))\(_n\)[GaH\(_2\)]\(_n\) (0 \(\leq x \leq 1\)) composed of [GaH\(_2\)]\(_n\)” anionic chains with a polyethylene structure.\(^10\) Remarkably, six indium atoms were previously found to arrange into one line upon the treatment of indium(I) iodide with a protonated \(N\)-xylyl \(\beta\)-diketiminate and a strong potassium base in tetrahydrofuran.\(^11\) Examples of the main-group homocatenated compounds are reported elsewhere.\(^12\) Noteworthy, thus far there have been no experimental reports on the Al
homocatenated compounds. The first remarkable example of a stable molecule with an 
Al–Al bond to be structurally characterized was $\text{R}_2\text{AlAlR}_2$ ($\text{R} = \text{CH(SiMe}_3)_2$).\textsuperscript{13} Later, a 
cyclic structure of the $\text{Al}_3\text{Cl}_3$ featuring direct Al–Al bonds was reported by matrix 
isolation technique using IR and Raman spectroscopies.\textsuperscript{14} The first “dialumininyne” 
($\text{Na}_2[\text{Ar}'\text{AlAlAr}']$) synthesized has been shown to have Al–Al bond with the bond order 
of 1.13.\textsuperscript{15} It was also found that “cycloaluminene” ($\text{Na}_2[(\text{AlAr}')_3]$) features somewhat 
weakened Al–Al $\sigma$ bonding, which is due the lone-pair character at the metal centers.\textsuperscript{15} 

Very recently, Gish et al.\textsuperscript{16} have theoretically predicted the existence of a new “Al 
homocatenated alkane” family $\text{Li}_n\text{Al}_n\text{H}_{2n+2}$, featuring striking similarities of the $\text{Al}_n\text{H}_{2n+2}$ 
kernel with their respective alkanes based on the electronic transmutation concept. In this 
communication we report a first experimental example of “Al homocatenated propane” 
$\text{Li}_2\text{Al}_3\text{H}_8^-$ species possessing direct Al–Al bonds arranged in a chain-like fashion.

Conceptually,\textsuperscript{6} a donation of one electron to Al atom might “transmute” it into 
Group 14 atoms. Thus, the theoretically proposed $\text{Li}_3\text{Al}_3\text{H}_8$ molecule was recently shown 
to be isostructural analogue of propane.\textsuperscript{16} Here we utilized anion photoelectron 
spectroscopy (PES) to test the viability of this hypothesis using the $\text{Li}_2\text{Al}_3\text{H}_8^-$ anion 
species, which is isoelectronic to the neutral $\text{Li}_3\text{Al}_3\text{H}_8$ cluster.

3-2. Experimental and computational methods

Anion photoelectron spectroscopy is conducted by crossing a mass-selected beam 
of negative ions with a fixed-frequency photon beam and energy-analyzing the resultant 
photodetached electrons. It is governed by the energy-conserving relationship, $h\nu = \text{EBE} + \text{EKE}$, where $h\nu$ is the photon energy, \text{EBE} is the electron binding (transition) energy,
and EKE is the electron kinetic energy. Our anion photoelectron spectrometer, which has been described previously, consists of one of many kinds of ion sources, a linear time-of-flight mass spectrometer, a mass gate, a momentum decelerator, a pulsed Nd:YAG photodetachment laser, and a magnetic bottle electron energy analyzer. Photoelectron spectra were taken with both 355 nm (3.49 eV) and 266 nm (4.66 eV) photon energies and calibrated against the well-known photoelectron spectrum of Cu$^{-}$.

Li$_2$Al$_3$H$_8^-$ cluster anions were generated in a laser vaporization source. Briefly, an aluminum rod was coated by a very thin layer of LiAlH$_4$ powder, and then ablated by a pulsed Nd:YAG laser beam operating at a wavelength of 532 nm. The resulting plasma was cooled by supersonically expanding a plume of helium gas from a pulsed gas valve (backing pressure of ~100 psi). Negatively charged anions were then extracted into the spectrometer prior to mass selection and photodetachment.

In order to find the most energetically favorable arrangement of atoms for the Li$_2$Al$_3$H$_8^-$ stoichiometry, we have utilized an unbiased search for the global minimum (GM) and low-energy isomers using the Coalescence Kick (CK) program to follow the geometry optimization procedure with the Gaussian 09 program. Exhaustive searches (30 thousand trial structures) for each multiplicity (singlet and triplet) were performed at the PBE0/LanL2DZ to initially explore the potential energy surface of Li$_2$Al$_3$H$_8^-$.

Afterwards, the low-lying isomers ($\Delta = 20$ kcal mol$^{-1}$) were recalculated using the more expansive 6-311++G(d,p) basis set (geometry optimization and follow-up frequency analyses to ensure that each structure is a minimum on the potential energy surface). Single-point coupled cluster calculations (CCSD(T)/aug-cc-pVTZ) at the DFT-optimized geometry were subsequently performed to give more precise relative energy
ordering. VDEs of isomer I of Li$_2$Al$_3$H$_8^-$ were calculated at three different levels of theory: TD-DFT, OVGF, and CCSD(T) (Table 3-1) and compared with experimental results. The chemical bonding analysis of the isomer I via Natural Bond Orbital (NBO) method at the PBE0/6-311++G(d,p) level of theory is also presented. Molekel 5.4.0.8 program was used for structural and molecular orbitals visualization.

3-3. Results and discussion

The photoelectron spectra of Li$_2$Al$_3$H$_8^-$ taken with 3.49 eV and 4.66 eV photon energies are presented in Fig. 3-1. Both spectra have an electron binding energy (EBE) band (X) starting from ~2.20 eV and peaking at 2.70 eV. In case of a sufficient Franck–Condon overlap between the ground state of the anion and the ground state of the neutral, and given there is not much hot band signal, the threshold of the first EBE band (~2.20 eV) should be the electron affinity (EA). The first experimental vertical detachment energy (VDE, an energy difference between an anion and the corresponding neutral species at the geometry of the anion), corresponding to the peak position, is 2.70 eV. The width of the band X suggests an appreciable geometry change between the ground state of Li$_2$Al$_3$H$_8^-$ and that of its neutral. In Fig. 3-1b, one can observe a second band (A) at the higher EBE end, which peaks at 4.32 eV that corresponds to the transition from the ground state of the anion to the first excited state of the neutral molecule.

Theoretically, twenty-eight isomers were found within 20 kcal mol$^{-1}$ range at PBE0/6-311++G(d,p) (Fig. 3-2). One can see that all of them are in singlet state; the lowest energy isomer in triplet state appears to be 28.4 kcal mol$^{-1}$ higher in energy than GM at CCSD(T). Interestingly, several low-lying isomers were found to have chiral
enantiomers. As we expected, the GM isomer I (Cs, 1A') was found to possess a propane-like geometry (Fig. 3-3) with the $R(\text{Al–Al}) = 2.68$ Å, similar to the corresponding bond length (2.67 Å)\(^{16}\) in its neutral isoelectronic analogue Li$_3$Al$_3$H$_8$. However, due to a different electrostatic field (different number of cations) in the global minimum structures of Li$_2$Al$_3$H$_8^-$ and Li$_3$Al$_3$H$_8$, locations of Li$^+$ cations in the first one is different than in the second one. Noteworthy, two closest in energy isomers (II and III in Fig. 3-3) adopt similar Al$_n$H$_{2n+2}$ kernels with somewhat different arrangement of Li atoms. Akin to the neutral Li$_3$Al$_3$H$_8$ molecule,\(^{16}\) the GM structure of Li$_2$Al$_3$H$_8^-$ maintains the structural features of propane better than any other isomers. Apparently, higher Al–H perturbation caused by Li cations (the weaker the lithium–hydrogen interaction, the shorter the Al–H σ bond) evokes some deviation from the propane-like framework, and, probably, overall system destabilization. Thus, isomers II and III are 7.2 kcal mol$^{-1}$ and 12.2 kcal mol$^{-1}$ higher in energy than isomer I at CCSD(T). It should be noted that the valence Al–Al–Al angle in Li$_2$Al$_3$H$_8^-$ (100.0°) is almost the same as in propane molecule (112.8°). Relative to the experimentally synthesized (Cs$_{10}$H[Ga$_3$H$_8$])\(^{9}\) and theoretically predicted (Li$_3$B$_3$H$_8$)\(^{6}\) X-homocatenated (X = B, Ga) propane-like species, Li$_2$Al$_3$H$_8^-$ cluster shows the smallest deviation in the valence angle from that of C$_3$H$_8$ molecule (Table 3-2).

To facilitate comparisons between the experimental and theoretical results, we calculated VDEs of isomer I of Li$_2$Al$_3$H$_8^-$ at three different levels of theory: TD-DFT,\(^{26}\) OVGF,\(^{27}\) and CCSD(T)\(^{24}\) (Table 3-1). We found that the VDEs computed using all these methodologies are in excellent agreement with the first two detachment channels observed in the experiment (Fig. 3-1). The electron detachment from 4a''-HOMO of the anion leads to a doublet final state for the neutral, thus giving rise to the first VDE of 2.78
eV (at CCSD(T)), compared with the experimental VDE of 2.70 eV (peak X). The next electron detachment from the 6a’-HOMO−1 produces the second theoretically calculated VDE of 4.21 eV, in excellent agreement with the experimental value of 4.32 eV corresponding to the peak A. Furthermore, the calculated adiabatic detachment energy (ADE, an energy difference between an anion and the corresponding neutral species at the geometry of the anion and a neutral species, respectively) of isomer I (2.28 eV at CCSD(T)/aug-cc-pVTZ//PBE0/6-311++G(d,p)) is also in excellent agreement with the experimentally measured ADE value of 2.20 eV. As expected, appreciable geometry changes upon the electron detachment from Li$_2$Al$_3$H$_8^-$ were observed for the neutral Li$_2$Al$_3$H$_8$ cluster (Table 3-3) consistent with the broad X band observed in the PES spectra (Fig. 3-1). We have also checked the VDEs of the second in energy isomer II (Table 3-1). However, the high relative energy of isomer II (Fig. 3-3), as well as its somewhat higher theoretical first VDE of 2.94 eV, makes this isomer unlikely to be populated in the molecular beam in any appreciable amount. Thus, we believe that the propane-like structure I is the only one contributing to the PES.

Results of the chemical bonding analysis of the isomer I via Natural Bond Orbital (NBO) $^{28}$ method at the PBE0/6-311G(d,p) level of theory are summarized in Fig. 3-4. According to the NBO results, the Li$_2$Al$_3$H$_8^-$ cluster has two direct two-center two-electron (2c-2e) Al–Al σ bonds with ON = 1.79 |e| and eight 2c-2e Al–H σ bonds with ON = 1.85–1.99 |e|. Li atoms are involved into the bonding primarily ionically, bearing charges of +0.49 and +0.56 (Table 3-4). These numbers are comparable to the existing studies on charge transfer from alkali metals to Al. $^{30}$ Al–H σ bonding is highly polarized towards hydrogen. On average, 70% of the electron density comes from hydrogen to
form Al–H σ bonds. It should be pointed out that the obtained chemical bonding picture for Li$_2$Al$_3$H$_8^-$ confirms the fact of Al homocatenation and is in perfect agreement with the NBO pattern revealed for propane molecule (Fig. 3-5). Although the positive charges on Li atoms are smaller than the ideal value of +1 according to the electronic transmutation principle, Al atoms gain enough electron density from lithium atoms to be able to transmute into Group 14 atoms and mimic the structural features of Group 14 hydrides.

3-4. Conclusions

In conclusion, thorough ab initio and PES studies of the Li$_2$Al$_3$H$_8^-$ cluster have reliably established the structure as well as deciphered the chemical bonding pattern of this unique species, thus introducing the first experimental example of Al homocatenation, yet unknown in chemistry. We hope that the current work will be of broad interest to scientists who are involved in synthesis of homocatenated chemical species across the Periodic Table as well as that our work will extend the view of chemical community on Al chemistry in particular.

References


20 M. J. Frisch, et al., Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford, CT, 2013.


29 U. Varetto, Molekel 5.4.0.8, Swiss National Supercomputing Centre, Manno, Switzerland, 2009.
Table 3-1 The observed vertical detachment energies (VDEs) for \( \text{Li}_2\text{Al}_3\text{H}_8^- \) and comparison with calculated VDEs for isomers I \((C_{ss}, \, ^1A')\) and II \((C_1, \, ^1A)\) at three levels of theory. All energies are in eV.

<table>
<thead>
<tr>
<th>Feature (Expt.)</th>
<th>Final state and electronic configuration</th>
<th>VDE (Theor.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td>TD-DFT(^a)</td>
</tr>
<tr>
<td></td>
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<td></td>
</tr>
<tr>
<td>Isomer I ((C_{ss}, , ^1A'))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>X</td>
<td>2.70 (2^A''\ldots(2a'')^2(3a')^2(5a')^2(6a')^2(4a'')^2)</td>
<td>2.67</td>
</tr>
<tr>
<td>A</td>
<td>4.32 (2^A'\ldots(2a')^2(3a')^2(5a')^2(6a')^2(4a')^2)</td>
<td>4.14</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.72</td>
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<tr>
<td></td>
<td></td>
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<td>5.98</td>
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<td></td>
<td>6.11</td>
</tr>
<tr>
<td>Isomer II ((C_1, , ^1A))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>X</td>
<td>2.70 (2^A\ldots(5a')^2(7a')^2(8a')^2(9a')^2(10a')^2)</td>
<td>2.82</td>
</tr>
<tr>
<td>A</td>
<td>4.32 (2^A\ldots(5a')^2(7a')^2(8a')^2(9a')^2(10a')^2)</td>
<td>4.19</td>
</tr>
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<td>5.68</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.20</td>
</tr>
</tbody>
</table>

\(^a\) VDEs were calculated at the TD-PBE0/aug-cc-pVTZ//PBE0/6-311++G(d, p) level of theory. The first VDE was calculated as the energy difference between the ground electronic state of the anion and the lowest doublet electronic state of the neutral at the geometry of the anion. Vertical excitation energies from the neutral states were then calculated and added to the first VDE to approximate the higher VDEs. (S2 values did not exceed their normal values by more than 2%).

\(^b\) VDEs were calculated at the OVGF/6-311++G(d, p)/PBE0/6-311++G(d, p) level of theory through the corrections to the orbital energies due to electron correlation and electron relaxation. (Pole-strength values were found to be more than 0.86).

\(^c\) VDEs were calculated at the CCSD(T)/aug-cc-pVTZ//PBE0/6-311++G(d, p) level of theory (NORM(A) values were found to be 1.14).

\(^d\) A value could not be calculated at this level of theory.
Table 3-2 Valence angle values (deg.) of propane and X-homocatenated propane-like species (X=B, Al, Ga) for C₃H₈, Li₃B₃H₈, Li₂Al₃H₈⁻, Li₂Al₃H₈, Li₃Al₃H₈, and Cs₁₀H[Ga₃H₈]₃.

<table>
<thead>
<tr>
<th></th>
<th>C₃H₈a</th>
<th>Li₃B₃H₈b</th>
<th>Li₂Al₃H₈a</th>
<th>Li₂Al₃H₈c</th>
<th>Li₃Al₃H₈c</th>
<th>Cs₁₀H[Ga₃H₈]₃d</th>
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</thead>
<tbody>
<tr>
<td>∠(Al-Al-Al)</td>
<td>112.8</td>
<td>116.0</td>
<td>100.0</td>
<td>90.7</td>
<td>92.5</td>
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<td>R(Al-Al)</td>
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<td></td>
</tr>
<tr>
<td>R(Li-Li)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R(Al₃-H₉)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R(Al₃-H₁₂)</td>
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<tr>
<td>R(Al₃-H₁₀)</td>
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<tr>
<td>R(Al₃-H₈)</td>
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</tr>
<tr>
<td>R(Al₃-H₆)</td>
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<td></td>
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</table>

a Calculated at the PBE0/6-311++G(d, p) levels of theory.
b From ref. 6.
c From ref. 15.
d From ref. 8.

Table 3-3 Comparison of geometrical characteristics of Li₂Al₃H₈⁻ and its neutral species at the PBE0/6-311++G(d, p) level of theory.

<table>
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<tr>
<th>Bond lengths (Å) and the valence angle (deg.)</th>
<th>Li₂Al₃H₈⁻</th>
<th>Li₂Al₃H₈</th>
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</thead>
<tbody>
<tr>
<td>∠(Al-Al-Al)</td>
<td>100.0</td>
<td>90.7</td>
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<tr>
<td>R(Al-Al)</td>
<td>2.68</td>
<td>2.75</td>
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<tr>
<td>R(Li-Li)</td>
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<td>3.81</td>
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<tr>
<td>R(Al₃-H₉)</td>
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<td>1.65</td>
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<tr>
<td>R(Al₃-H₁₂)</td>
<td>1.62</td>
<td>1.59</td>
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<tr>
<td>R(Al₃-H₁₀)</td>
<td>1.71</td>
<td>1.65</td>
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<tr>
<td>R(Al₃-H₈)</td>
<td>1.70</td>
<td>1.67</td>
</tr>
<tr>
<td>R(Al₃-H₆)</td>
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<td>1.59</td>
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Table 3-4 NPA charges on atoms of the global minimum structure I of Li$_2$Al$_3$H$_8^-$ at the PBE0/6-311++G(d, p) level of theory.

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<th>Atoms</th>
<th>NPA charge</th>
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<tr>
<td>Li$_1$</td>
<td>0.56241</td>
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<tr>
<td>Li$_2$</td>
<td>0.48642</td>
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<tr>
<td>Al$_3$</td>
<td>0.35786</td>
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<td>Al$_4$</td>
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</tr>
<tr>
<td>Al$_5$</td>
<td>-0.02440</td>
</tr>
<tr>
<td>H$_6$</td>
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<tr>
<td>H$_7$</td>
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<tr>
<td>H$_8$</td>
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<tr>
<td>H$_9$</td>
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<tr>
<td>H$_{10}$</td>
<td>-0.38540</td>
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<tr>
<td>H$_{11}$</td>
<td>-0.38540</td>
</tr>
<tr>
<td>H$_{12}$</td>
<td>-0.31882</td>
</tr>
<tr>
<td>H$_{13}$</td>
<td>-0.31882</td>
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Fig. 3-1 Photoelectron spectra of Li$_2$Al$_3$H$_8^-$. (a) At 355 nm (3.496 eV) and (b) at 266 nm (4.661 eV).

<table>
<thead>
<tr>
<th>Isomer</th>
<th>Symmetry</th>
<th>Energy (eV)</th>
<th>ZPE Corrected Energy (eV)</th>
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<td>I</td>
<td>C$_p$ 1'A</td>
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<td>[0.0]</td>
</tr>
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<td>[7.2]</td>
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<tr>
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<td>[11.0]</td>
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</tr>
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<td>[18.2]</td>
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<tr>
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<td>C$_p$ 1'A</td>
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<td>[15.6]</td>
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<tr>
<td>XXIII</td>
<td>C$_p$ 1'A</td>
<td>19.7</td>
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Fig. 3-2 Optimized isomers of Li$_2$Al$_3$H$_8^-$ (Δ=20 kcal mol$^{-1}$), their point group symmetries, spectroscopic states, and ZPE corrected relative energies at the PBE0/6-311++G(d, p) and CCSD(T)/aug-cc-pVTZ/PBE0/6-311++G(d, p) (in square brackets) levels of theory.
Fig. 3-3 Lowest energy isomers of Li$_2$Al$_3$H$_8^-$, their point group symmetries, ground electronic states, and ZPE corrected relative energies (in kcal mol$^{-1}$) at the PBE0/6-311++G(d,p) and CCSD(T)/aug-cc-pVTZ/PBE0/6-311++G(d,p) (in square brackets) levels of theory. The solid rods between atoms help visualization and do not necessarily represent 2c-2e σ bonds here and elsewhere. H is blue, Al is yellow, and Li is magenta.

Fig. 3-4 Visualization of the NBO results for the Li$_2$Al$_3$H$_8^-$ cluster. (a) Two aluminum–aluminum 2c-2e σ bonds (shown superimposed, left) (b) eight aluminum–hydrogen 2c-2e σ bonds (shown superimposed, right). ON denotes occupation number.

Fig. 3-5 The ground electronic state, point group symmetry and NBO results for propane molecule: two 2c-2e C–C σ bonds (center, shown superimposed) and eight 2c-2e C–H σ bonds (right, shown superimposed).
CHAPTER 4

COBALT-CENTRED BORON MOLECULAR DRUMS WITH THE HIGHEST
COORDINATION NUMBER IN THE CoB\textsubscript{16}\textsuperscript{-} CLUSTER\textsuperscript{1}

Abstract

The electron deficiency and strong bonding capacity of boron have led to a vast variety of molecular structures in chemistry and materials science. Here we report the observation of highly symmetric cobalt-centered boron drum-like structures of CoB\textsubscript{16}\textsuperscript{-}, characterized by photoelectron spectroscopy and \textit{ab initio} calculations. The photoelectron spectra display a relatively simple spectral pattern, suggesting a high symmetry structure. Two nearly degenerate isomers with D\textsubscript{8d} (I) and C\textsubscript{4v} (II) symmetries are found computationally to compete for the global minimum. These drum-like structures consist of two B\textsubscript{8} rings sandwiching a cobalt atom, which has the highest coordination number known heretofore in chemistry. For the first time we show that doping of boron clusters with a transition metal atom induces an earlier two-dimensional to three-dimensional structural transition. The CoB\textsubscript{16}\textsuperscript{-} cluster has been tested as a building block in a triple-decker sandwich, suggesting a promising route for its realization in the solid state.

Boron, the fifth element in the Periodic Table, possesses such diverse chemical structures and bonding that are second only to carbon. Bulk boron consists of connected three-dimensional (3D) cages in many of its allotropes\textsuperscript{1,2} and boron-rich borides\textsuperscript{3,4}. However, for isolated clusters it was computationally shown\textsuperscript{5,6} that icosahedral cage...

structures of B\textsubscript{12} and B\textsubscript{13} were unstable, even though they were initially proposed as possible candidates for these two clusters\textsuperscript{7}. Over the past decade, small anionic boron clusters have been systematically characterized both experimentally and theoretically to exhibit planar or quasi-planar structures in their ground states up to B\textsubscript{27}\textsuperscript{−,8-10}. Recent works show that anionic boron clusters continue to be two-dimensional (2D) at B\textsubscript{30}\textsuperscript{−,11}, B\textsubscript{35}\textsuperscript{−,12}, and B\textsubscript{36}\textsuperscript{−,13}. The 2D-to-3D transition was suggested to occur at B\textsubscript{20}\textsuperscript{14} for neutral and at B\textsubscript{16}\textsuperscript{+} for cationic clusters\textsuperscript{15}. Very recently it is shown that the transition from 2D to fullerene-like 3D structures occurs in negatively charged boron clusters at about forty boron atoms in B\textsubscript{39}\textsuperscript{−} (ref. 16) and B\textsubscript{40}\textsuperscript{−} (ref. 17). Due to the nearly spherical shapes of these clusters, they have been named borospherenes. Doping boron clusters with a single metal atom opens a new avenue to create clusters with novel structures and chemical bonding. It has been experimentally observed that various transition metal atoms can be placed inside of monocyclic boron rings to form beautiful molecular wheel-type structures (M©B\textsubscript{n})\textsuperscript{18}, following an electronic design principle inspired by the doubly $\sigma$ and $\pi$ aromatic B\textsubscript{9}\textsuperscript{−} cluster\textsuperscript{19}. It was shown that the Nb©B\textsubscript{10}\textsuperscript{−} and Ta©B\textsubscript{10}\textsuperscript{−} clusters possess the record coordination number of 10 in the planar environment for the central metal atom\textsuperscript{20}. These clusters have pushed the limits of structural chemistry.

Here we report the observation of a large metal-doped boron cluster of CoB\textsubscript{16}\textsuperscript{−}, which is produced using a laser vaporization cluster source and characterized by photoelectron spectroscopy (PES). Extensive computational searches reveal that there are two nearly degenerate structures for CoB\textsubscript{16}\textsuperscript{−}, which are indistinguishable at the highest level of theory employed. They both possess tubular double-ring framework and give similar photoelectron spectral patterns. The structures can be viewed as two B\textsubscript{8} rings
sandwiching a Co atom, reminiscent of a drum and giving rise to the highest coordination number known in chemistry thus far.

4-1. Results

4-1.1. Experimental results

The photoelectron spectra of CoB$_{16}^-$ at two photon energies are displayed in Fig. 4-1. The lowest binding energy band (X) represents the electron detachment transition from the anionic ground state to that of neutral CoB$_{16}$. The higher binding energy bands, A, B, ..., denote detachment transitions to the excited states of neutral CoB$_{16}$. The vertical detachment energies (VDEs) for all observed bands are given in Table 4-1, where they are compared with the calculated VDEs.

The 266 nm spectrum (Fig. 4-1a) reveals three well-resolved PES bands for CoB$_{16}^-$. The band X gives rise to a VDE of 2.71 eV. The adiabatic detachment energy (ADE) for band X was evaluated from its onset to be 2.48 eV, which also represents the electron affinity of neutral CoB$_{16}$. The width of band X suggests an appreciable geometry change between the ground electronic state of CoB$_{16}^-$ and the ground electronic state of CoB$_{16}$. Following a relatively large energy gap, an intense and broad band A is observed at a VDE of 3.45 eV and a close-lying band B at a VDE of 3.78 eV. The 193 nm spectrum (Fig. 4-1b) shows nearly continuous signals beyond 4 eV. The sharp spikes above 5 eV in the high binding side of the 193 nm spectrum are due to statistical noises because of low electron counts. An intense and broad band C is clearly observed at a VDE of 4.86 eV. Two more bands can be tentatively identified at higher binding energies, D (VDE: ~5.3 eV) and E (VDE: ~5.6 eV). Overall, the PES spectral pattern is relatively
simple, suggesting that the framework of the CoB$_{16}^-$ cluster is likely to have high
symmetry.

4-1.2. Theoretical results and comparison with experiment

Extensive structural searches were initially done at the PBE0/3-21G level of
theory with the follow-up calculations (Δ= 25 kcal mol$^{-1}$) at the PBE0/Def2-TZVP level
of theory, which led to two similar drum-like structures: isomer I (D$_{8d}$, $^3A_2$) and isomer II
(C$_{4v}$, $^1A_1$) identified as the global minima for CoB$_{16}^-$ (Fig. 4-2). These two highly
symmetric structures, consisting of a central Co atom sandwiched by two B$_8$ monocyclic
rings, are found to be almost degenerate at various levels of theory (Fig. 4-3). Clearly, the
method dependency of predicting relative energies of the low-lying structures for CoB$_{16}^-$
suggests the importance of comparison with experiment in determining the global
minimum. We previously studied how optimized geometries of small boron clusters
differed at DFT and CCSD(T) levels of theory.$^{21,22}$ We found that B3LYP/6-311+G*
geometries are quite close (within 0.03 Å between nearest boron atoms) to those at the
CCSD(T)/6-311+G* level of theory. We also compared the geometries of boron clusters
at PBE0/6-311+G* and B3LYP/6-311+G*, and found that they are also very close.$^{23}$
Therefore, PBE0/3-21G level of theory was used for the preliminary search and
PBE0/Def2-TZVP for the final optimized geometries of CoB$_{16}^-$. The highest level of
theory employed (ROCCSD(T)/6-311+G(2df)//PBE0/Def2-TZVP) (this abbreviation
means that single point energy calculations were performed at ROCCSD(T)/6-311+G(2df)
using optimized UPBE0/Def2-TZVP geometries here and elsewhere) indicates 1.4 kcal
mol$^{-1}$ energy difference including zero-point energy corrections (Fig. 4-3). This small
value is in the range of the theoretical errors for such a complex transition-metal-doped boron cluster. Therefore, isomers I and II should be considered to be degenerate based on our calculations. Fig. 4-2 shows the small differences in bond distances between isomers I and II; the latter is not significantly distorted from the D$_{8d}$ symmetry. The B-B bond lengths of the B$_8$ rings for both isomers are in the range of 1.55-1.63 Å, similar to the corresponding values (1.56 Å) in the Co©B$_8^-$ molecular wheel$^{18}$. The nearest isomer III (C$_2$, 1A) is 8.7 kcal mol$^{-1}$ higher in energy at the ROCCSD(T) method and represents a distorted drum-like structure composed of two B$_7$ rings with two B atoms outside the drum (Fig. 4-3). In fact, the majority of the low-lying isomers within 20 kcal mol$^{-1}$ (Fig. 4-3) represent various derivatives (drum-like or possessing principal geometrical features of the drum-like structure) of isomers I and II, showing the stability of the drum-like structures. It should be noted that there are significant bonding interactions between the two B$_8$ rings and between the Co atom and all 16 B atoms in both isomers I and II (vide infra). Interestingly, the drum structure in a quintet state (isomer XIV in Fig. 4-3) appears to be the most stable one out of all other quintet isomers. It should be mentioned that there were two previous DFT calculations on similar drum-like structures of neutral boron clusters doped with transition metal atoms$^{24,25}$.

To facilitate comparisons between the experimental and theoretical results, we calculated low-lying VDEs of isomers I and II of CoB$_{16}^-$ using three methods (Table 4-1). We found that the VDEs computed using the two DFT methods are not very impressive; but we observed good agreement between the theoretical VDEs at ROCCSD(T)/6-311+G(2df) and the experimental data for the first two detachment channels (Table 4-1). Since isomer I is open-shell, the electron detachment energy from the doubly degenerate
4e_2-HOMO should lead to a doublet final state for the neutral. The computed VDE at ROCCSD(T) is 2.59 eV, compared with the experimental VDE of 2.71 eV. The next electron detachment from the non-degenerate 2b_2-HOMO-1 should lead to both a quartet and a doublet final state, with the quartet being lower in energy. The calculated VDE for the quartet final state at ROCCSD(T) is 3.28 eV, compared with the VDE of the A band at 3.45 eV. Unfortunately, we were not able to calculate any higher VDEs because of the limitation of the ROCCSD(T) method. However, we believe that the good agreement between experiment and theory for the first two VDEs provides sufficient credence for the identified drum-like isomer I for the CoB_{16}^{-} cluster.

Isomer II gives very similar theoretical VDEs as isomer I at all three levels of theory, consistent with the similarities in their geometries. Since isomer II is a closed-shell species, we were able to calculate only the first VDE value at the ROCCSD(T) method as 2.61 eV, also in good agreement with the experimental data. Furthermore, the calculated ADEs of isomer I (2.45 eV) and isomer II (2.43 eV) (PBE0/Def2-TZVP) are in excellent agreement with the experimentally measured ADE value of 2.48 eV. We should point out that there is a Jahn-Teller distortion for the neutral CoB_{16} drum-like structure of isomer I, consistent with the broad X band observed in the PES spectra (Fig. 1). Indeed, the calculated relaxed neutral CoB_{16} structure I^0 (Fig. 4-4) has lower symmetry (C_{2v}), as one would expect for the Jahn-Teller distorted structure due to the occupation of the doubly degenerate HOMO (4e_2) of isomer I by a single electron. In fact, the HOMO (4b_2) of isomer II originates from the HOMO (4e_2) of isomer I when one of the doubly degenerate orbitals is doubly occupied. Therefore, the detachment of one electron from the doubly occupied HOMO (4b_2) of isomer II leads to the same neutral
structure I\textsuperscript{b}. The high relative energy of isomer III, as well as its appreciably higher theoretical first VDE of 3.65 eV (Table 4-2), makes this cluster unlikely to be populated in the molecular beam in any appreciable amount.

4-2. Discussion

Tubular (or drum-like) boron clusters have been of interest for many years, because they can be considered as the embryos for boron nanotubes\textsuperscript{14}. However, such drum-like structures have never been observed experimentally for bare boron clusters, even though they have been shown to be stable computationally\textsuperscript{14,26-29}. For instance, the B\textsubscript{20} cluster was first suggested as the global minimum on the basis of theoretical calculations\textsuperscript{14}, but it has not been observed or confirmed experimentally\textsuperscript{29}. Tubular structures were also studied for the bare B\textsubscript{16}\textsuperscript{+}, B\textsubscript{16}, B\textsubscript{16}\textsuperscript{−}, and B\textsubscript{16}\textsuperscript{2−} species\textsuperscript{15,30}. For the B\textsubscript{16}\textsuperscript{+} cationic cluster, the tubular structure was suggested to be the global minimum\textsuperscript{15}, whereas the tubular structures of both B\textsubscript{16} and B\textsubscript{16}\textsuperscript{−} were found to be high-energy isomers\textsuperscript{30}. Clearly, the strong coordination interactions with the Co atom significantly stabilize the tubular B\textsubscript{16} to give the drum-like global minima (structures I and II) for CoB\textsubscript{16}−. Bare anionic boron clusters are found to be 2D up to B\textsubscript{36}− (ref. 13), while some transition-metal-doped anionic boron clusters are found to preserve the planar boron framework upon metal doping\textsuperscript{31,32}. The largest experimentally observed metal-doped boron cluster (CoB\textsubscript{12}−) maintains a similar planar geometry for the B\textsubscript{12} moiety\textsuperscript{32}. Hence, the doping of the Co atom induces an earlier 2D-to-3D transition for boron clusters, as shown by the 3D isomers I and II of CoB\textsubscript{16}−. In fact, the CoB\textsubscript{16}− drum structure represents the highest coordination number known in chemistry today. The previous
highest coordination number known experimentally was 15 for \([\text{Th(H}_3\text{BNMe}_2\text{BH}_3])_4\)\(^{33}\), though theoretical studies have suggested the highest coordination numbers of 15 in \(\text{PbHe}_{15}^{2+}\) (ref. 34) and 16 in the Friauf–Laves phases in \(\text{MgZn}_2\) or \(\text{MgNi}_2\) (ref. 35). Endohedral fullerenes \((\text{M}@\text{C}_{60})\) have been observed\(^{36,37}\), but the metal atom in those cases interacts with the \(\text{C}_{60}\) shell primarily ionically and it does not stay in the center of \(\text{C}_{60}\).

It is interesting to point out that the B-B distances in the \(\text{B}_8\) rings of both isomers I and II of \(\text{CoB}_{16}^-\) and the bare tubular \(\text{B}_{16}\) are very similar (Table 4-3). To gain insight into the chemical bonding of the \(\text{CoB}_{16}^-\) drums, we performed chemical bonding analyses for isomers I and II using the AdNDP method\(^{38}\), which is an extension of the popular Natural Bond Orbital (NBO) method\(^{39}\). It should be noted that the bonding in some double-ring tubular boron clusters has been discussed previously\(^{9,40,41}\).

Since isomer I has two unpaired electrons, we used the unrestricted AdNDP (UAAdNDP) analysis, which enables treatments of the \(\alpha\) and \(\beta\) electrons separately. To obtain an averaged result for a bond (Fig. 4-5), we added the UAAdNDP results for the \(\alpha\) and \(\beta\) electrons of the same type of bonds. According to the UAAdNDP analysis results, the 58 valence electrons in \(\text{CoB}_{16}^-\) can be divided into four sets. The first set (Fig. 4-5a,b) consists of localized bonding elements, while the other three sets (Fig. 4-5c-g, h-j, k-o) are composed of delocalized bonding elements. In the first set, the UAAdNDP analysis for isomer I revealed the following localized bonding elements: one electron lone pair (1c-2e bond) (Fig. 4-5b) of \(3d_z^2\)-type on Co with an occupation number (ON) of 1.98 \(|e|\) and sixteen 2c-2e B-B \(\sigma\)-bonds (Fig. 4-5a) with ON = 1.84 \(|e|\) within each \(\text{B}_8\) ring (all superimposed onto the \(\text{B}_{16}\) fragment in Fig. 4-5), which can also be viewed as 3c-2e
bonds with the ON=1.96 |e| responsible for the bonding between the boron rings. In the last case, a boron atom from the neighboring ring contributes somewhat (0.12 |e|) to the formation of the 3c-2e σ-bond. The 2c-2e B-B σ-bonds are very similar to the peripheral B-B bonds found in all 2D boron clusters\textsuperscript{8-10}. The second set includes five delocalized σ bonds (denoted as σ+σ), which are formed from delocalized σ bonds between the two B\textsubscript{8} rings. Since the σ orbitals between the two boron rings overlap positively, we designate them as σ+σ in the second set, which constitutes σ-aromaticity according to the 4n + 2 (n = 2) Hückel rule. The three delocalized 16c-2e σ+σ bonds (Fig. 4-5c-e) with ON = 1.82-1.86 |e| involve only σ-bonding within the boron rings, whereas the two delocalized 17c-2e σ+σ bonds (Fig. 4-5f-g) come primarily from the 3d\textsubscript{xy} and 3d\textsubscript{x\textsuperscript{2}-y\textsuperscript{2}} AOs of Co interacting with the boron rings. It should be noted that the direct covalent interactions between Co and the B\textsubscript{16} unit via the 3d\textsubscript{xy} and 3d\textsubscript{x\textsuperscript{2}-y\textsuperscript{2}} AOs of Co are found to be around 0.6 |e| according to the AdNDP analysis. The third set (Fig. 4-5h-j) shows three delocalized σ-σ bonds, which represent bonding interactions within each ring, but antibonding interactions between the two boron rings. This set of delocalized bonds also constitutes σ-aromaticity according to the 4n + 2 (n = 1) Hückel rule. In the third set, the 16c-2e σ-σ bond (Fig. 4-5h) involves mainly the two boron rings, whereas the two 17c-2e σ-σ bonds (Fig. 4-5i-j) involve interactions between the 3d\textsubscript{xz} and 3d\textsubscript{yz} AOs of Co with the boron rings. The direct covalent interaction of the 3d\textsubscript{xz} and 3d\textsubscript{yz} AOs of Co with the boron kernel is assessed to be around 0.5 |e|. The last set includes five delocalized bonds, which represent π-π interactions between the boron rings: three 16c-2e π-π bonds (Fig. 4-5k-m) with ON = 1.98-2.00 |e| and two 16c-1e π-π bonds (Fig. 4-5n,o) with ON = 1.00 |e| (one unpaired electron on each bond). The eight π electrons in the last set suggest π-
aromaticity according to the $4n$ rule ($n = 2$) for triplet states. Therefore, the stability of isomer I of CoB$_{16}^-$ can be considered to be due to the double $\sigma$- and $\pi$-aromaticity and bonding interactions of the 3d AOs of Co with the B$_8$ rings.

As expected, isomer II of CoB$_{16}^-$, which is close in energy and geometry to isomer I, has almost the same bonding pattern as that of isomer I (Fig. 4-6). All the bonding elements found in isomer I are also found in isomer II except for the last set (Fig. 4-6k-n). Since isomer II is closed-shell, eight electrons in the last set are observed to form four 16c-2e $\pi$-$\pi$ bonds with $\text{ON} = 1.98$-$2.00$ |e|, rendering this isomer $\pi$-antiaromatic. Hence, isomer II exhibits conflicting aromaticity ($\sigma$-aromatic and $\pi$-antiaromatic), which leads to the some distortion to $C_{4v}$ symmetry compared to the $D_{8d}$ symmetry of the doubly aromatic isomer I. As was mentioned earlier, the HOMO (4b$_2$) of isomer II originates from the HOMO (4e$_2$) of isomer I when one of the doubly degenerate orbitals is doubly occupied. Indeed, occupation of only one degenerate MO by two electrons causes the electronic instability, which causes the geometric rearrangement of isomer II lowering the $D_{8d}$ symmetry to $C_{4v}$.

To understand the interactions between Co and the tubular B$_{16}$ host, we have performed AdNDP analyses for the neutral B$_{16}$ tubular isomer (Fig. 4-7). Similar to isomers I and II of CoB$_{16}^-$, the AdNDP analyses give sixteen 2c-2e B-B $\sigma$-bonds with ON values of 1.70 |e| within the two B$_8$ rings. The encapsulation of Co strengthens the B-B $\sigma$-bonds within each B$_8$ ring in CoB$_{16}^-$, but weakens the inter-ring interactions, compared to the bare B$_{16}$, as reflected by their ON values (Fig. 4-5 and Fig. 4-7) and the B-B bond lengths (Table 4-3). The remaining 16 electrons in B$_{16}$ participate in delocalized bonding: five 16c-2e $\sigma^+\sigma$ bonds and three 16c-2e $\pi$-$\pi$ bonds, rendering the
tubular $B_{16}$ doubly $\sigma$- and $\pi$-aromatic. The major difference in chemical bonding between
the drum-like $B_{16}$ and $CoB_{16}^{-}$ comes from two factors: 1) the formation of an additional
set (Fig. 4-5h-j) of the delocalized $\sigma$-$\sigma$ bonds in $CoB_{16}^{-}$; and 2) participation of Co 3d
AOs in the two 17c-2e $\sigma$+$\sigma$ bonds (Fig. 4-5f,g). Both factors are consistent with structural
changes between $CoB_{16}^{-}$ and $B_{16}$. There are strong bonding interactions between Co and
the $B_{16}$ host in $CoB_{16}^{-}$ to stabilize the tubular $B_{16}$ structure, because the global minimum
of $B_{16}$ is planar$^{30}$.

Isomer I of $CoB_{16}^{-}$ is open-shell with two unpaired electrons, whereas isomer II
can be viewed as a result of Jahn-Teller distortion from isomer I. Addition of two
electrons to isomers I or II would create a closed-shell and doubly aromatic $CoB_{16}^{3-}$
species with $D_{8d}$ symmetry. Our calculations indeed confirmed this hypothesis: $CoB_{16}^{3-}$
was found to be a minimum on the potential energy surface with very similar bond
distances as in isomer I (Table 4-3). The triply charged $CoB_{16}^{3-}$ species can be
electronically stabilized by charge transfers from alkali atoms, such as in $Na_{2}CoB_{16}^{-}$.
Since ligation would be needed to ultimately synthesize $CoB_{16}^{-}$, we considered a triple-decked $[CoB_{16}(CaCp)_{2}]^{-}$ sandwich complex (Fig. 4-8), using the divalent Ca atoms and
the aromatic $C_{5}H_{5}^{-} (Cp^{-})$ ligands. It should be mentioned that similar $[CpLiB_{6}LiCp]^{2-}$
triple-decked complex$^{42}$ with the double antiaromatic $B_{6}^{2-}$ unit was previously suggested
to be stable and viable experimentally. We found that the $[CoB_{16}(CaCp)_{2}]^{-}$ triple-decked
complex was a minimum on the potential energy surface with high electronic stability.
All the B-B and Co-B bond lengths were found to be almost the same as in isomers I and
II of $CoB_{16}^{-}$ (Table 4-3). We have further performed AdNDP analyses and found that the
triple-decked sandwich complex exhibits exactly the same chemical bonding pattern as
the parent CoB$_{16}^-$ (Figs. 4-9-4-11). The NPA charge on Ca was found to be +1.54, consistent with the initial hypothesis and the charge-transfer nature of the triple-decked [CoB$_{16}$(CaCp)$_2$]$^-$ sandwich complex. Thus, the CoB$_{16}^-$ molecular drum can serve as a building block for the design of novel cluster-assembled nanomaterials. The high stability of the CoB$_{16}^-$ drum structures may also help the search for new metal-boride phases containing various boron ring units$^{43}$.

We have produced and characterized a large Co-doped boron cluster, CoB$_{16}^-$, using photoelectron spectroscopy and quantum-chemical calculations. Extensive computational searches established two high symmetry (D$_{8d}$ and C$_{4v}$) drum-like structures with Co sandwiched by two B$_8$ rings as nearly degenerate global minima. The CoB$_{16}^-$ molecular drums represent the highest coordination for a metal atom known in chemistry and opens new possibilities for designing novel boron-based nanomaterials. First, the CoB$_{16}^-$ drums may be considered as the embryo to make filled boron nanotubes due to the significant B-B bonding between the two B$_8$ rings. Second, there are possibilities to observe larger doped-boron clusters with even higher coordination number to further push the limit of coordination number in chemistry. Third, we have demonstrated one possibility to use CoB$_{16}^-$ as a building block of new cluster-assembled nanomaterials in a triple-decked complex.

4-3. Methods

4-3.1. Experimental Methods

The experiment was carried out using a magnetic-bottle PES apparatus equipped with a laser vaporization cluster source$^{44}$. Briefly, the CoB$_{16}^-$ anion clusters were
produced by laser vaporization of a cold-pressed target composed of Co and isotopically enriched $^{11}$B. Bismuth was added as a binder and it also provided a convenient calibrant (Bi$^-$) for the PES experiment. Clusters formed in the nozzle were entrained in a He carrier gas and underwent a supersonic expansion to form a collimated cluster beam. The He carrier gas was seeded with 5% Ar for better cooling of the entrained clusters$^{22}$. The anionic clusters were extracted from the collimated cluster beam and analyzed by a time-of-flight mass spectrometer. The CoB$_{16}^-$ anion clusters were mass-selected and decelerated before being photodetached by a laser beam at 193 nm (6.424 eV) from an ArF excimer laser or 266 nm (4.661 eV) from a Nd:YAG laser. Photoelectrons were collected at nearly 100% efficiency by a magnetic bottle and analyzed in a 3.5 m long flight tube. The resolution of the apparatus, $\Delta E_k/E_k$, was about than 2.5%, i.e., ~25 meV for 1 eV electrons.

### 4-3.2. Theoretical Methods

Search for the global minimum of CoB$_{16}^-$ was performed using the Coalescence Kick (CK) program$^{45}$ at the PBE0/3-21G level of theory$^{46,47}$. The CK algorithm generated approximately 10,000 trial structures for each spin multiplicity (singlet, triplet, and quintet), followed by geometry optimization. Low-lying isomers within 25 kcal mol$^{-1}$ were further refined at a more expansive basis set, Def2-TZVP$^{48}$. For each structure, vibrational frequencies were calculated and imaginary frequencies were followed to ensure that the isomer corresponded to a true minimum on the potential energy surface. Spin-contamination was found to be less than 10 % in all DFT calculations. For selected isomers, we performed additional geometry optimization at various DFT levels, as well
as more accurate single-point coupled-cluster calculations [ROCCSD(T)/6-311+G(2df)], in order to reliably establish the relative energy ordering. Vertical detachment energies (VDEs) of the three lowest energy structures were calculated at three different methods [UPBE0, UB3LYP, and ROCCSD(T)] to compare with the experimental data. The VDEs were obtained as the difference in energy between the ground state of the anion and selected low-lying electronic states of the neutral molecule at the geometry of the anion. All calculations were done using GAUSSIAN-0949.

To understand the chemical bonding, we carried out electron localization analyses using the Adaptive Natural Density Partitioning (AdNDP) method38 at the PBE0/6-31G(d) level of theory. Previously, AdNDP results have been shown to be insensitive to the level of theory or basis set used50. The AdNDP analysis is based on the concept of electron pairs as the main elements of chemical bonds. It represents the molecular electronic structure in terms of \( n \)-center two-electron (\( nc-2e \)) bonds, recovering the familiar lone pairs (1c-2e) and localized 2c-2e bonds or delocalized \( nc-2e \) bonds (\( 3 \leq n \leq \text{total number of atoms in the system} \)). The MOLEKEL 5.4.0.8 program51 is used for molecular structure and AdNDP bond visualizations.

References


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### Table 4-1 | Experimental and theoretical vertical electron detachment energies (VDEs) in eV of CoB$_{16}^-$

<table>
<thead>
<tr>
<th>VDE (exp.)$^a$</th>
<th>Isomer I</th>
<th>Isomer II</th>
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<tr>
<td></td>
<td>(1a$_t^2$1e$_t^4$1e$_t^4$1b$_t^2$1e$_t^7$2e$_t^4$2a$_t^2$1e$_t^4$2e$_t^2$)</td>
<td>(1a$_t^2$1e$_t^4$1b$_t^2$1b$_t^2$2a$_t^2$2e$_t^3$3a$_t^5$2b$_t^2$2e$_t^2$)</td>
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<tr>
<td>MO VDE (theo.)</td>
<td>MO VDE (theo.)</td>
<td>MO VDE (theo.)</td>
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<tr>
<td>----------------</td>
<td>-----------------</td>
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<tr>
<td>X 2.71(5)</td>
<td>4e$_t^2$</td>
<td>2.58</td>
</tr>
<tr>
<td>A 3.45(3)</td>
<td>2b$_t^2$</td>
<td>2.97</td>
</tr>
<tr>
<td>B 3.78(3)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>C 4.86(5)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>D 5.3(1)</td>
<td>—</td>
<td>—</td>
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<tr>
<td>E 5.6(1)</td>
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$^a$ Numbers in parentheses indicate the uncertainties of the last digit. The ADE of the X band is measured to be 2.48(5) eV.

$^b$ The VDEs were calculated at the UPBE0/6-311+G(2df)/UPBE0/Def2-TZVP level of theory. Spin-contamination was found to be very small.

$^c$ The VDEs were calculated at the UB3LYP/6-311+G(2df)/UPBE0/Def2-TZVP level of theory. Spin-contamination was found to be very small.

$^d$ The VDEs were calculated at the ROCCSD(T)/6-311+G(2df)/PBE0/Def2-TZVP level of theory, because the UHF wave function has a very high spin-contamination.

$^e$ VDE could not be calculated at this level of theory.
Table 4-2 | The first two calculated VDE values for isomer III (C2, 1A) of CoB16− at three levels of theory.

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<thead>
<tr>
<th>Isomer III (1a^22a^1b^23a^2b^24a^3b^25a^2b^26a^2b^27a^28a^29a^210a^29b^212a^210b^213a^214a^211b^212b^215a^213b^216a^2)</th>
<th>UPBE\textsuperscript{a}</th>
<th>UB3LYP\textsuperscript{b}</th>
<th>ROCCSD(T)\textsuperscript{c}</th>
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<tr>
<td>MO</td>
<td>VDE</td>
<td>MO</td>
<td>VDE</td>
</tr>
<tr>
<td>16a</td>
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<td>16a</td>
<td>3.32</td>
</tr>
<tr>
<td>13b</td>
<td>3.62</td>
<td>13b</td>
<td>3.53</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The VDEs were calculated at the UPBE/6-311+G(2df)/UPBE/Def2-TZVP level of theory. Spin-contamination was found to be very small.

\textsuperscript{b} The VDEs were calculated at the UB3LYP/6-311+G(2df)/UPBE0/Def2-TZVP level of theory. Spin-contamination was found to be very small.

\textsuperscript{c} The VDEs were calculated at the ROCCSD(T)/6-311+G(2df)/PBE0/Def2-TZVP level of theory, because the UHF wave function has a very high spin-contamination.

\textsuperscript{d} VDE could not be calculated at this level of theory.

Table 4-3 | Comparison of the bond distances in B\textsubscript{16}, CoB\textsubscript{16}− (isomers I and II), and [CoB\textsubscript{16}(CaCp)\textsubscript{2}]\textsuperscript{−} clusters at PBE0/Def2-TZVP. All values are in Å.

<table>
<thead>
<tr>
<th></th>
<th>B\textsubscript{16}</th>
<th>CoB\textsubscript{16} (structure I\textsuperscript{b})</th>
<th>CoB\textsubscript{16}− (isomer I)</th>
<th>CoB\textsubscript{16}− (isomer II)</th>
<th>[CoB\textsubscript{16}(CaCp)\textsubscript{2}]\textsuperscript{−}</th>
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</thead>
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<td>R(Co-B)</td>
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<tr>
<td>R(peripheral B-B)</td>
<td>1.63</td>
<td>1.57-1.60</td>
<td>1.59</td>
<td>1.55-1.63</td>
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<td>R(B-B between the rings)</td>
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<td>1.76-1.81</td>
<td>1.80</td>
<td>1.78-1.87</td>
<td>1.80</td>
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</table>
**Figure 4-1 | Photoelectron spectra.** Photoelectron spectra (a) at 266 nm (4.661 eV) and (b) at 193 nm (6.424 eV) of CoB$_{16}^-$. 
Figure 4-2 | Two views of isomer I (a) and isomer II (b) of the CoB$_{16}^-$ cluster. Their point group symmetries and spectroscopic states are shown in parenthesis. Sticks drawn between atoms help visualization and do not necessarily represent classical 2c-2e B–B or Co–B bonds here and elsewhere. All distances are in Å.
Figure 4-3 | Relative energies (in kcal mol$^{-1}$) of the lowest lying (<20 kcal mol$^{-1}$ above the global minimum) isomers of CoB$_{16}^-$ at the PBE0/Def2-TZVP level of theory. B3LYP/Def2-TZVP, TPSSh/Def2-TZVP, and ROCCSD(T)/6-311+G(2df)//PBE0/Def2-TZVP relative energies for the three lowest energy isomers I, II, and III are shown in parenthesis, square brackets, and curly brackets, respectively. All energies are corrected for zero-point energies (ZPE) at their respective levels of theory aside from single-point coupled-cluster calculations, which are ZPE corrected at PBE0/Def2-TZVP. The C$_{4V}$ structure (isomer II$^d$) has one imaginary frequency at this level of theory. Geometry optimization following the imaginary frequency leads to the local minimum structure possessing C$_4$ symmetry. However, including ZPE corrections the vibrationally averaged structure has effectively C$_{4V}$ symmetry.
Figure 4-4 | Two views of the neutral CoB₁₁ isomer 1⁰. Its point group symmetries and spectroscopic states are shown in parenthesis. All distances are in Å.
Figure 4-5 | The overall chemical bonding picture (a-o) obtained for the isomer I of the CoB\textsubscript{16} molecular drum via the UAdNDP analysis. ON denotes occupation number here and elsewhere.
Figure 4-6 | The AdNDP chemical bonding picture obtained for isomer II (C_4v, 1A_1) of CoB_{16}^-.
Figure 4-7 | The AdNDP chemical bonding picture obtained for the tubular isomer of the B₁₆ cluster.

Figure 4-8 | Two views of the triple-decked [CoB₁₆(CaCp)₂]⁻ cluster. Its point group symmetry and spectroscopic state are shown in parenthesis. Color scheme: Ca is green, C is grey, H is blue, B is red, and Co is magenta.
Figure 4-9 | Localized elements of chemical bonding: 1c-2e (lone pairs) and 2c-2e (classical two-center two-electron) bonds found on both the CoB$_{16}^-$ and C$_3$H$_5^-$ fragments.
Figure 4-10 | Delocalized elements of chemical bonding found on the CoB$_{16}^{3-}$ fragment in [CoB$_{16}$(CaCp)$_2$]$^-$. 
Figure 4-11 | Delocalized elements of chemical bonding found on the $\text{C}_3\text{H}_5^-$ fragments in $[\text{CoB}_{16}(\text{CaCp})_2]^-$.
CHAPTER 5
ASSESSING THE VIABILITY OF EXTENDED NONMETAL ATOM CHAINS IN

\[ \text{M}_n\text{F}_{4n+2} \quad (\text{M}=\text{S AND Se}) \]

Abstract

Theoretical investigations to evaluate the viability of extended nonmetal atom chains on the basis of molecular models with the general formula \( \text{M}_n\text{F}_{4n+2} \) (M=S and Se) and corresponding solid-state systems exhibiting direct S–S or Se–Se bonding were performed. The proposed high-symmetry molecules were found to be minima on the potential energy surface for all \( \text{S}_n\text{F}_{4n+2} \) systems studied (\( n=2–9 \)) and for selenium analogues up to \( n=6 \). Phonon calculations of periodic structures confirmed the dynamic stability of the \( -(\text{SF}_4–\text{SF}_4)_x \) chain, whereas the analogous \( -(\text{SeF}_4–\text{SeF}_4)_x \) chain was found to have a number of imaginary phonon frequencies. Chemical bonding analysis of the dynamically stable \( -(\text{SF}_4–\text{SF}_4)_x \) structure revealed a multicenter character of the S–S and S–F bonds. A novel definition and abbreviation (ENAC) are proposed by analogy with extended metal atom chain (EMAC) complexes.

Cotton and co-workers introduced the chemical concept of extended metal atom chain (EMAC) complexes.\(^1\) The first purple compound \([\text{Ni}_3(\text{dpa})_4\text{Cl}_2]\) (dpa\(^-\) = dipyridylamido anion) containing three Ni atoms was first reported in 1968.\(^2\) However its correct structure was established only in 1991.\(^3\) This structure contains a linear chain, Cl–Ni–Ni–Ni–Cl, surrounded by a spiral set of four dpa ligands. Since then similar

compounds with three metal atoms, such as Cu, Co, Cr, and other transition metals, connected in a triatomic chain have been reported.\[^4\] Tri-, tetra-, penta-, hepta-,\[^1,5\] nona-,\[^6\] deca-,\[^7\] and hendecanuclear\[^8\] EMACs surrounded by oligo-α-pyridylamino ligands have been synthesized and studied. In principle, it is thought that it would be possible to extend the system to an infinite one-dimensional molecule.\[^7\] The trinuclear complex \([\text{[Pt(Me}_2\text{Bpy})_2]\text{[PtCl}_2(\text{Me}_2\text{Bpy})_2]]^{2+}\) (Me\(_2\)Bpy=4,4'-dimethyl-2,2'-bipyridine) with Pt–Pt–Pt bonds has been shown to have relatively strong (about 40 kcal mol\(^{-1}\)) Pt–Pt metallic bonds with similar covalent and ionic contributions.\[^9\] A huge number of other linear metal chains are known, such as Li\(_2\)Sb\[^10\] with two linear Sb chains and Au\(_2\)MP\(_2\) compounds (M=Hg, Pb, Tl) possessing Hg, Tl, and Pb chains.\[^11\] As well as linear chains, different helical (Sb chains\[^12\] in the crystal structure of K\(_2\)Sb) and zigzag chains (P chains\[^11\] in Au\(_2\)MP\(_2\) (M=Hg, Pb, Tl) compounds; Sb chains\[^13\] in the structure of CaSb\(_2\); Ge chains\[^14\] in the structure of DyGe\(_3\)) have also been reported. Progress made in the preparation and characterization of EMAC complexes has been reviewed.\[^15\]

The number of molecules containing linear chains of nonmetal atoms is significantly smaller. Carbyne, an allotrope of carbon that forms large monoatomic linear chains with alternate single and triple carbon–carbon bonds, has a long history in chemistry.\[^16\] Boron, by acquiring an extra electron, forms unbranched linear monoatomic chains of boron atoms surrounded by lithium cations.\[^17\] Linear phosphorus–boron chains\[^18\] and double-helical lithium–phosphorous\[^19\] chains have been studied theoretically. It was reported that there are two phases with helical structures made up of triangular and squared chains of sulfur that are stable at 1.5 GPa and temperatures from 300 to 1100 K.\[^20\] Interestingly, selenium can also form the helical squared chain
structures in a similar way to sulfur. Analogous oxygen helical structures are also found under the pressure of metallization. The crystal structures of TeF$_4$, SeF$_4$ and more recently SF$_4$ have been reported. Notably, in all these tetrafluorides, there is no direct M–M bonding (M=Te, Se, S).

Herein we present the computational results for M$_{2n}$F$_{4n+2}$ molecules (M=S, Se) with a monoatomic chain structure based on direct S–S or Se–Se bonding. We refer to these species as extended nonmetal atom chain (ENAC) compounds by analogy with extended metal atom chain (EMAC) complexes.

According to our calculations, the staggered structure I with $D_{4d}$ symmetry is a true minimum on the potential energy surface (PES), in agreement with the experimental data (Figure 5-1). We performed the search (ca. 2500 trial structures) for the global minimum and low-lying isomers of S$_2$F$_{10}$ by the Coalescence Kick method and found out that there were no other unfragmented isomers that were more stable than isomer I. In fact, the most stable isomer existed as two distinct parts: octahedral SF$_6$ and SF$_4$ with a seesaw shape. Interestingly, two other close-lying isomers, which were also fragmented, were found to be very high in energy (see Figure 5-2). The eclipsed structure TS1 with $D_{4h}$ symmetry is a first-order saddle point on the PES and corresponds to a barrier of 9.6 kcal mol$^{-1}$ (DFT) or 9.1 kcal mol$^{-1}$ (CCSD(T)) for rotation about the S–S σ bond.

The experimentally determined distance $R$(S–S)=2.274(5) Å in S$_2$F$_{10}$ is appreciably longer than the corresponding distance in S$_2$H$_2$: $R$(S–S)=2.055 Å, which suggests the presence of a single S–S σ bond. Since the S–S distance is quite dependent on the electronegativity of X in S$_2$X$_2$ species (X=H, Li, Na, F, Cl, Br, I), as was recently shown by El-Hamdi et al., the S–S distance in S$_2$F$_{10}$ was also compared with that in
Experimental data show a slightly decreased value \((R(S-S)=1.888 \text{ Å})\),\[29\] although the bond order is expected to be the same as in \(S_2H_2\). The values for the \(S-S\) bond-dissociation energy (BDE) of \(S_2F_{10}\), \(S_2H_2\), and \(S_2F_2\) were found to be 41.8, 66.6, and 77.3 kcal mol\(^{-1}\), respectively, thus confirming the bond weakening in \(S_2F_{10}\), which is partly due to F···F repulsion and sulfur–fluorine electron transfer.\[30\]

Chemical bonding analysis of \(S_2F_{10}\) performed by Natural Bond Orbital (NBO)\[31,32\] and Adaptive Natural Density Partitioning (AdNDP)\[33\] methods (see Figure 5-3c) revealed that the \(S-F_{eq}\) and \(S-F_{ax}\) bonds are classical with occupation number (ON) values close to the ideal value of 2.00 \(|e|\), whereas the \(S-S\) \(\sigma\) bond has a rather low ON value of 1.45 \(|e|\) (NBO) or 1.58 \(|e|\) (AdNDP). According to NBO analysis, every 2\(c\)–2\(e\) \(S-F\) bond is formed by 3s3p\(^3\)3d\(^2\) hybrid atomic orbitals (AOs) of sulfur and primarily 2p AOs of fluorine with a small contribution of 2s AOs. Since those bonds are highly polarized towards fluorine (only about 20% of the electron density comes from sulfur), the resulting occupation of 3d AOs is rather small. NBO analysis also revealed that valence non-Lewis density is 2.08 \(|e|\) (2.53% of the valence electron density), which is a sign of some multicenter contribution to the bonding. Since the NBO method requires and maintains strict local (and global) orthogonality between all NBOs, the only way to make five \(S-F\) bonds and one \(S-S\) bond whose S hybrids are orthogonal and pointed towards the vertices of an octahedron is by placing d-character in the hybrids. Thus, the d-character appears as a result of orthogonalization. The occupation of 3d orbitals can be evaluated from the composition of 10 \(S-F\) bonds and one \(S-S\) bond. According to our calculations, the occupation of the 3d AOs of S is 0.90 \(|e|\). This value is substantially higher than the corresponding value found by natural electron configuration (NEC).
analysis, which is completely independent from the natural population analysis in the bonding description. NEC analysis for the S$_2$F$_{10}$ molecule shows the following occupation on the S atom: 3s$^{1.14}$ 3p$^{2.30}$ 4s$^{0.01}$ 3d$^{0.18}$, which proves little involvement of d orbitals in the active valence space. In general, this kind of problem can occur when a delocalized system is forced to be described by a single localized configuration. Therefore, we believe that both S–S and S–F bonds should be described by the multicenter bonding. AdNDP analysis allowed us to search for the 3c–4e bonding on the F$_{eq}$–S–F$_{eq}$ fragments. Indeed, we found that eight equatorial fluorine atoms can be described by 3c–4e bonds with an ON value of 2.00 |e| (see Figure 5-3d). Within the AdNDP method we could also search for a 12-centered 2-electron (12c–2e) σ bond instead of the 2c–2e S–S σ bond. This user-directed approach showed that the ON of the 12c–2e σ bond is 2.00 |e| with about 0.4 |e| distributed among equatorial fluorine atoms with antibonding character (see Figure 5-3d). This result is consistent with S–S σ-bond elongation and weakening in S$_2$F$_{10}$ relative to S$_2$H$_2$ and S$_2$F$_2$ (see Figure 5-3 for comparative illustrations of chemical bonding in S$_2$H$_2$, S$_2$F$_2$, and S$_2$F$_{10}$).

Our calculations showed that S$_2$F$_{10}$ is not thermodynamically stable towards dissociation into SF$_6$+SF$_4$ by 23.3 kcal mol$^{-1}$ at the DFT level and by 27.7 kcal mol$^{-1}$ at CCSD(T)/cc-pVTZ//M06-2X/6-311+G(2df). These numbers provide us with some insight on the expected errors for larger systems. These results are in agreement with the experimental observation$^{[34]}$ that S$_2$F$_{10}$ decomposes slowly in an inert container above 150°C into SF$_6$+SF$_4$ (see Figure 5-4). By following the dissociation path, we found the SF$_6$–SF$_4$ transition state TS2 (see Figure 5-5). The barrier for the S$_2$F$_{10}$→SF$_6$+SF$_4$ process is 66.4 kcal mol$^{-1}$ at the DFT level and corresponds to TS2. Thus, this
thermodynamically unstable molecule is very stable kinetically. We found that all \(\text{S}_n\text{F}_{4n+2}\) molecules studied \((n=2–9; \text{see Figure } 5-6)\) in \(D_{4d}\) (even \(n\)) and \(D_{4h}\) (odd \(n\)) conformations are minima on the PES, although all of them are thermodynamically unstable towards the \(\text{S}_{n-1}\text{F}_{4(n-1)+2} + \text{SF}_4\) dissociation channel (see Table 5-1).

We also searched for possible alternative structures of the proposed chain-like structures along the series \(\text{S}_n\text{F}_{4n+2}\) \((n=2–9)\), in which direct S–S bonding is expected, but failed to find any structures lower in energy that corresponded to a minimum on the PES. Calculation of the periodic boundary conditions (PBCs) for the \(-(\text{SF}_4–\text{SF}_4)_\infty-\) system resulted in the following geometrical parameters: \(R(\text{S–S})=2.36\ \text{Å} \text{ and } R(\text{S–F})=1.62\ \text{Å} \) (CASTEP); \(R(\text{S–S})=2.38\ \text{Å} \text{ and } R(\text{S–F})=1.63\ \text{Å} \) (VASP). Both bonds are slightly longer than those in molecular species: the S–S bond was found to be longer than that in \(\text{S}_2\text{F}_{10}\) \((2.274\ \text{Å})\), and the S–F bonds appear to be longer than the mean S–F bond length in \(\text{S}_2\text{F}_{10}\) \((1.569\ \text{Å})\) and in \(\text{SF}_6\) \((1.5623\ \text{Å})\).[35]

We also performed PBC calculations for the molecular crystal of \(\text{SF}_4\), which has the space group \(P2_12_12_1\) according to experimental data.[24] It turned out that the molecular crystal of \(\text{SF}_4\) is more stable than our \(-(\text{SF}_4–\text{SF}_4)_\infty-\) system by 21.7 kcal mol\(^{-1}\) per \(\text{SF}_4\) group. This result is consistent with our calculations for the molecular species (see Table 5-1), for which the dissociation energy for the \(\text{S}_n\text{F}_{4n+2} \rightarrow \text{S}_{n-1}\text{F}_{4(n-1)+2} + \text{SF}_4\) channel was found to be approximately 22 kcal mol\(^{-1}\). A plot of phonon dispersions in the Brillouin zone (see Figure 5-7) showed that no imaginary phonon frequency is observed in the whole Brillouin zone, thus indicating the dynamic stability of the \(-(\text{SF}_4–\text{SF}_4)_\infty-\) linear chain.
For chemical bonding analysis of the periodic system, we utilized a newly developed solid-state AdNDP (SSAdNDP) algorithm\(^{[36]}\) in conjunction with general and user-directed searches. The resulting picture is shown in Figure 5-8b. Similar to the results derived for the S\(_2\)F\(_{10}\) molecule, the use of SSAdNDP enabled direct classical S–F and S–S σ bonds to be found with ON values of 1.96 and 1.61 |e|, respectively. However, according to NEC analysis, the S atom has the following occupation of orbitals: 

\[
3s^{1.44}3p^{2.48}4s^{0.01}3d^{0.17},
\]

which is very similar to that of S\(_2\)F\(_{10}\). Therefore, we believe that the initially found eight 2c–2e S–F bonds should be described as four 3c–4e bonds in the F\(_{eq}\)–S–F\(_{eq}\) fragments shown in Figure 5-8b as a combination of bonding and nonbonding orbitals. User-directed SSAdNDP analysis enabled a 10c–2e bond (with eight fluorine atoms included within one unit cell) to be found instead of a 2c–2e S–S σ bond. This approach gave us an ON (10c–2e bond) value of 1.98 |e|, which shows that approximately 0.4 |e| is distributed among fluorine atoms with antibonding character, similar to the situation in S\(_2\)F\(_{10}\). Importantly, the AdNDP results derived for the molecular S\(_n\)F\(_{4n+2}\) systems (\(n=2–9\)) are also in agreement with the SSAdNDP calculations.

Although we are not aware of any experimental data on the Se\(_2\)F\(_{10}\) molecule, our calculations show that the staggered \(D_{4d}\) structure I is a true minimum on the PES. The eclipsed TS3 structure corresponds to a torsional barrier of 4.7 kcal mol\(^{-1}\) at the DFT level (see Figure 5-9).

The Se–Se BDE of Se\(_2\)F\(_{10}\) was found to be 27.9 kcal mol\(^{-1}\), whereas the Se–Se BDE values of Se\(_2\)H\(_2\) and Se\(_2\)F\(_2\), in which a single Se–Se σ bond is expected, are 51.0 and 60.1 kcal mol\(^{-1}\), respectively, thus also confirming the bond weakening in Se\(_2\)F\(_{10}\). These
values are supported by the corresponding bond lengths: $R(\text{Se–Se})=2.47$ Å in Se$_2$F$_{10}$, $R(\text{Se–Se})=2.33$ Å in Se$_2$H$_2$, $R(\text{Se–Se})=2.20$ Å in Se$_2$F$_2$.

Initial AdNDP and NBO analyses of Se$_2$F$_{10}$ show that Se–F$_{\text{eq}}$ and S–F$_{\text{ax}}$ σ bonds are classical with ON(Se–F$_{\text{eq}}$)=1.95–2.00 |e| and ON(Se–F$_{\text{ax}}$)=2.00 |e|, whereas the Se–Se σ bond has a rather low ON value of 1.33 |e| (NBO) or 1.51 |e| (AdNDP). Similar to the S$_2$F$_{10}$ molecule, we believe that the chemical bonding in Se$_2$F$_{10}$ should be described by multicenter bonding: 3c–4e bonding on the F$_{\text{eq}}$–Se–F$_{\text{eq}}$ fragments and a 12c–2e bond instead of a 2c–2e Se–Se σ bond. Again, the low ON of the Se–Se σ bond in Se$_2$F$_{10}$ is in concordance with its elongation and weakening relative to those in Se$_2$H$_2$ and Se$_2$F$_2$.

We also found that the Se$_2$F$_{10}$ molecule is not thermodynamically stable by 31.4 kcal mol$^{-1}$ at the DFT level and dissociates into SeF$_6$+SeF$_4$ (see Figure 5-10). The barrier for the Se$_2$F$_{10}$→SeF$_6$+SeF$_4$ process is 45.6 kcal mol$^{-1}$ at the DFT level and corresponds to TS4 (see Figure 5-11). Similar to the S$_2$F$_{10}$ molecule, thermodynamically unstable Se$_2$F$_{10}$ is very stable kinetically.

Geometry optimizations of the Se$_n$F$_{4n+2}$ molecules revealed that high-symmetry molecules containing a linear chain of Se atoms are minima on the PES up to $n=6$. At $n=7$, the high-symmetry structures are no longer minima, since the F$_4$ fragments are slightly shifted relative to each other, thus resulting in lower symmetry ($C_4$, $D_4$ geometries; see Figure 5-12). In spite of this irregularity, the Se–Se σ-bond lengths remain almost the same upon chain elongation (see Table 5-2). It was found that all the Se$_n$F$_{4n+2}$ molecules studied were thermodynamically unstable towards the Se$_{n-1}$F$_{(n-1)\times 2}$+SeF$_4$ dissociation channel with about the same energy value of around 30 kcal mol$^{-1}$ (see Table 5-2).
The proposed infinitely long one-dimensional -(SeF$_4$–SeF$_4$)$_\infty$ system was found to possess the following geometrical parameters: $R$(Se–Se)=2.58 Å and $R$(Se–F)=1.76 Å (CASTEP), and $R$(Se–Se)=2.64 Å and $R$(Se–F)=1.78 Å (VASP). Although the proposed high-symmetry Se$_n$F$_{4n+2}$ molecules ($n=2$–$6$) were shown to be local minima on the PES, the phonon-density-of-states calculations revealed a number of imaginary phonon frequencies for -(SeF$_4$–SeF$_4$)$_\infty$, thus showing its dynamic instability. Despite its instability, we performed SSAdNDP analysis on -(SeF$_4$–SeF$_4$)$_\infty$ for comparison with the results obtained for its sulfurous analogue.

In conclusion, we have computationally assessed the viability of M$_n$F$_{4n+2}$ molecules (M=S, Se; $n=2$–$9$) as well as infinitely long chains based on direct S–S or Se–Se bonding and surrounded by fluorine atoms. We found that these molecules are not thermodynamically stable with respect to the $M_nF_{4n+2}\rightarrow M_{n-1}F_{4(n-1)+2}+MF_4$ dissociation channel. However, high-energy barriers for the $M_2F_{10}\rightarrow MF_6+MF_4$ processes cause us to believe that these ENAC compounds are also viable species. We propose a novel definition and, consequently, a novel abbreviation (ENAC) by analogy with EMAC complexes. PBC calculations confirm the dynamic stability of the -(SF$_4$–SF$_4$)$_\infty$ chain. For this chain, no imaginary phonon frequency was observed in the whole Brillouin zone, whereas the analogous -(SeF$_4$–SeF$_4$)$_\infty$ chain was found to have plenty of imaginary phonon frequencies. We hope that our results will inspire experimentalists to synthesize these interesting one-dimensional chemical species.
References


[42] Gaussian 09 (Revision B.0.1), M. J. Frisch, et al., Gaussian, Inc., Wallingford CT, **2009**.


[53] U. Varetto, *Molekel 5.4.0.8*, Swiss National Supercomputing Centre, Manno (Switzerland).
### Tables and Figures

**Table 5-1.** Calculated properties of $S_n F_{4n+2}$ molecules at the M06-2X/6-311+G(2df) level of theory.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>R($S$-$S$), Å</th>
<th>$\Delta E$, kcal mol$^{-1}$</th>
<th>HOMO-LUMO gap, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_2 F_{10}$, $^1A_1 (D_{4d})$</td>
<td>2.26</td>
<td>-23.3</td>
<td>10.34</td>
</tr>
<tr>
<td>$S_3 F_{14}$, $^1A_{1g} (D_{4h})$</td>
<td>2.26</td>
<td>-21.9</td>
<td>9.54</td>
</tr>
<tr>
<td>$S_4 F_{18}$, $^1A_1 (D_{4d})$</td>
<td>2.26</td>
<td>-22.1</td>
<td>9.28</td>
</tr>
<tr>
<td>$S_5 F_{22}$, $^1A_{1g} (D_{4h})$</td>
<td>2.26</td>
<td>-22.1</td>
<td>9.19</td>
</tr>
<tr>
<td>$S_6 F_{26}$, $^1A_1 (D_{4d})$</td>
<td>2.26</td>
<td>-22.0</td>
<td>9.15</td>
</tr>
<tr>
<td>$S_7 F_{30}$, $^1A_{1g} (D_{4h})$</td>
<td>2.26</td>
<td>-22.0</td>
<td>9.13</td>
</tr>
<tr>
<td>$S_8 F_{34}$, $^1A_1 (D_{4d})$</td>
<td>2.26</td>
<td>-22.1</td>
<td>9.12</td>
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<tr>
<td>$S_9 F_{38}$, $^1A_{1g} (D_{4h})$</td>
<td>2.26</td>
<td>-22.0</td>
<td>9.10</td>
</tr>
</tbody>
</table>

$^1$Dissociation energy for the $S_n F_{4n+2} \rightarrow S_{n-1} F_{4(n-1)+2} + SF_4$ channel.

**Table 5-2.** Calculated properties of $Se_n F_{4n+2}$ molecules at the M06-2X/6-311+G(2df) level of theory.

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<th>Molecule</th>
<th>R($Se$-$Se$), Å</th>
<th>$\Delta E$, kcal mol$^{-1}$</th>
<th>HOMO-LUMO gap, eV</th>
</tr>
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<tbody>
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<td>$Se_2 F_{10}$, $^1A_1 (D_{4d})$</td>
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<td>-31.4</td>
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<td>2.46</td>
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<td>$Se_4 F_{18}$, $^1A_1 (D_{4d})$</td>
<td>2.46</td>
<td>-29.7</td>
<td>7.80</td>
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<td>-29.6</td>
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<td>$Se_7 F_{30}$, $^1A_{1g} (D_{4h})$</td>
<td>2.46</td>
<td>-30.7</td>
<td>7.60</td>
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<td>$Se_8 F_{34}$, $^1A_1 (D_{4d})$</td>
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<td>-30.9</td>
<td>7.59</td>
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<td>$Se_9 F_{38}$, $^1A_{1g} (D_{4h})$</td>
<td>2.46</td>
<td>-30.2</td>
<td>7.57</td>
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</tbody>
</table>

$^1$Dissociation energy for the $Se_n F_{4n+2} \rightarrow Se_{n-1} F_{4(n-1)+2} + SeF_4$ channel.
Figure 5-1. Molecular structures of the staggered (I) and eclipsed (TS1) structures of S$_2$F$_{10}$ at 0 K and their relative energies (in kcal mol$^{-1}$) at M06-2X/6-311+G(2df) and CCSD(T)/cc-pVTZ//M06-2X/6-311+G(2df) (shown in square brackets), both corrected for zero-point energies at the DFT level.

Figure 5-2. Representative isomers of S$_2$F$_{10}$ and their relative energies (corrected for zero-point energies) at the M06-2X/6-311+G(2df) level of theory.
Figure 5-3. AdNDP results of chemical bonding in a) S₂H₂, b) S₂F₂ and c) S₂F₁₀ at the M06-2X/6-311+G(2df) level of theory (six lone pairs (six 1c-2e bonds) with ON=1.97-2.00 [e] on two fluorine atoms in S₂F₂ and thirty lone pairs with ON=1.97-1.99 [e] on ten fluorine atoms in S₂F₁₀ are not shown for clarity). d) Multicenter representation of eight 2c-2e S–F<sub:eq</sub> σ bonds via four 3c-4e F<sub:eq</sub>–S–F<sub:eq</sub> bonds and 2c-2e S–S σ bond via the 12c-2e bond.
**Figure 5-4.** Dissociation products of the S$_2$F$_{10}$ molecule: SF$_6$ (left) and SF$_4$ (right).

**Figure 5-5.** SF$_6$-SF$_4$ transition state TS2 corresponding to the saddle point on the PES.
Figure 5-6. $S_nF_{4n+2}$ molecules ($n=2-9$) in $D_{4d}$ (even $n$) and $D_{4h}$ (odd $n$) conformations corresponding to local minima on the PES and their optimized bond lengths ($\text{Å}$) at the M06-2X/6-311+G(2df) level of theory.
Figure 5-7. Phonon dispersion of the infinite \((\text{SF}_4-\text{SF}_4)_\infty\) chain. The structure is stable to distortions hence a local minimum.
Figure 5-8. a) Structure of the infinite -(SF₄–SF₄)ₙ- system with the corresponding unit cells and b) representative bonds identified by SSAdNDP analysis: one 10c-2e bond, one 3c-4e Fₑq–S–Fₑq bond. A total of 24 lone pairs (1c-2e bonds) on eight fluorine atoms within one unit cell with ON=1.94-1.98 |e| are omitted for clarity.
Figure 5-9. Molecular structures of the staggered (I) and eclipsed (TS3) structures of Se$_2$F$_{10}$ at 0 K and their relative energies at M06-2X/6-311+G(2df) corrected for zero-point energies (in kcal mol$^{-1}$).

Figure 5-10. Dissociation products of the Se$_2$F$_{10}$ molecule: SeF$_6$ (left) and SeF$_4$ (right).

Figure 5-11. SeF$_6$-SeF$_4$ transition state TS4 corresponding to the saddle point on the PES.
Figure 5-12. SeₙF₄ₙ₊₂ molecules \((n=2-6)\) in \(D_{4d}\) (even \(n\)) and \(D_{4h}\) (odd \(n\)) conformations and lower symmetry SeₙF₄ₙ₊₂ molecules \((n=7-9)\) corresponding to local minima on the PES (two projections showing the lowering of high symmetry) with their optimized bond lengths (Å) at the M06-2X/6-311+G(2df) level of theory.
Abstract

We analyzed chemical bonding in graphene using fragmental approach, the Adaptive Natural Density Partitioning method, electron sharing indices and nucleus independent chemical shift indices. We proved that graphene is aromatic, but its aromaticity is different from aromaticity in benzene, coronene, or circumcoronene. Aromaticity in graphene is local with two $\pi$-electrons delocalized over every hexagon ring. We believe that the developed chemical bonding picture for graphene will be helpful for understanding chemical bonding in defects such as point defects, single-, double- and multiple vacancies, carbon adatoms, foreign adatoms, substitutional impurities, and new materials that are derivatives of graphene.

6-1. Introduction

The recent discovery of graphene [1, 2], a one-atom-thick planar sheet of carbon atoms that are densely packed in a honeycomb crystal lattice gave us the opportunity to probe properties of two-dimensional (2D) materials. The isolated layers of graphene were found to have many unusual properties such as high carrier mobilities (>200 000 cm$^2$·Vs$^{-1}$ at electron densities of $2 \times 10^{11}$ cm$^{-2}$) [3–6], exceptional Young modulus values (>0.5–1 TPa), and large force constants (1–5 N·m$^{-1}$) [7–9]. Due to these properties

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graphene is attractive for many potential commercial applications such as energy storage [10], micro- and optoelectronics [11].

Understanding of chemical bonding in graphene is crucial for rationalizing different kinds of defects such as point defects, single-, double- and multiple vacancies, carbon adatoms, foreign adatoms, substitutional impurities [12], and new materials that are derivatives of graphene. While σ-bonding in graphene is assumed to be a rigid honeycomb framework built out of two-center two-electron (2c–2e) C–C σ-bonds, the π-bonding is supposed to be delocalized. Delocalized bonding in benzene and other polycyclic hydrocarbons is usually interpreted in terms of aromaticity introduced in chemistry by Kekulé [13–15]. He associated aromaticity with the presence of C₆ units in aromatic compounds. Thus, according to him, similarity to benzene was essential for a compound to be aromatic. Aromaticity is associated with planarity and enhanced chemical stability, compared to similar non-aromatic molecules. Unlike the nonaromatic molecules containing double carbon–carbon bonds, which undergo electrophilic addition reactions, aromatic molecules do not engage in such addition reactions. Instead they undergo electrophilic aromatic substitution and nucleophilic aromatic substitution reactions. The Hückel 4n+2 π-electrons rule [16] governs the electronic counting for aromatic molecules. According to Moran et al. [17] graphite is an ultimate expression of prototypical aromatic molecule benzene with the higher resonance energy per π-electron. They analyzed aromaticity in the four series of polybenzenoid hydrocarbons (PBH): (1) (C₂₄H₁₂, C₅₄H₁₈, C₉₆H₂₄, C₁₅₀H₃₀, C₂₁₆H₃₆), (2) (C₄₂H₁₈, C₇₈H₃₀, C₁₁₄H₃₀, C₁₈₆H₄₂), (3) (C₂₂₂H₄₂), and (4) (C₄₈H₂₄, C₁₃₈H₄₂) using nucleus-independent chemical shift (NICS) index [18]. They concluded that NICS indices predicted aromaticity in all individual
hexagon rings in Series 2 and 3 PBHs. Series 1 and 4 PBHs were more difficult to summarize since they include structures with moderately diatropic rings and/or adjacent aromatic rings. Thus, they did not reach the number of hexagons in the PBH molecules, where there is a uniform magnetic shielding field.

6-2. Results and discussion

In this article we present a chemical bonding analysis of graphene using fragmental approach, which has been very successful in interpretation of chemical bonding in the most stable 2D-lattice of boron (α-sheet) [19] computationally predicted by Tang and Ismail-Beigi [20, 21] and Yang, Ding and Ni [22]. For our chemical bonding analysis we selected three fragments: $\text{C}_6\text{H}_6^{4+}$, $\text{C}_{24}\text{H}_{12}^{10+}$, and $\text{C}_{54}\text{H}_{18}^{16+}$ (Fig. 6-1).

The external charges on our fragments were selected in order to preserve the number of $\pi$-electrons in the infinite graphene lattice. In the infinite graphene lattice every carbon atom belongs to three adjacent hexagons, thus, only 1/3 of its $\pi$-electron belongs to a particular hexagon resulting in two $\pi$-electrons per hexagon. Indeed, our $\text{C}_6\text{H}_6^{4+}$, $\text{C}_{24}\text{H}_{12}^{10+}$ and $\text{C}_{54}\text{H}_{18}^{16+}$ fragments have 2, 14, and 38 $\pi$-electrons respectively, in agreement with the expected number of $\pi$-electrons in the system. In all our models we used a fixed C–C distance of 1.42 Å (experimentally determined for graphite [23]) and a C–H distance of 1.10 Å. We performed chemical bonding analysis on graphene model fragments using adaptive natural density partitioning (AdNDP) method recently developed by Zubarev and Boldyrev [24]. This method has been successfully used to analyze chemical bonding in boron clusters [24], aromatic organic molecules [25], gold clusters [26] and the all-boron α-sheet. It was previously shown [25–27] that the results
of AdNDP do not depend significantly on the basis set. The results of our AdNDP analysis for C₆H₆⁴⁺ are summarized in Fig. 6-2.

The simplest C₆H₆⁴⁺ fragment has six C–H classical σ-bonds, six C–C classical σ-bonds, and one completely delocalized 6c–2e π-bond. Our AdNDP results for C₂₄H₁₂¹⁰⁺ are presented in Fig. 6-3. The coronene-like fragment has thirty 2c–2e C–C and 12 2c–2e C–H classical σ-bonds, and seven 6c–2e π-bonds. This analysis shows a very different chemical bonding picture from that previously found for a neutral coronene C₂₄H₁₂ [25]. According to that analysis, neutral coronene has two globally delocalized π-concentric systems with first six electrons delocalized over the central hexagon and with another six π-electrons delocalized over the eighteen-atom external ring. This globally delocalized π-concentric bonding was also found by Fowler and co-workers [28–30], who showed that there is a paratropic ring current on the six-carbon hub and a diatropic ring current on the eighteen-carbon ring. Our π-bonding for the C₂₄H₁₂¹⁰⁺ fragment is very different from the π-bonding in coronene, since we have a local aromaticity with two π-electrons localized over every hexagon ring.

The results of the AdNDP analysis for the C₅₄H₁₈¹⁶⁺ fragment are shown in Fig. 6-4. According to our AdNDP analysis the C₅₄H₁₈¹⁶⁺ fragment has 72 2c–2e C–C and 18 2c–2e C–H classical σ-bonds, and 19 6c–2e π-bonds. The π-bonding for the C₅₄H₁₈¹⁶⁺ fragment is also different from the π-bonding in the neutral circumcoronene C₅₄H₁₈. In our description, we have a local aromaticity with two π-electrons localized over every hexagon ring with occupation number (ON) values of 1.83–1.88 |e|, while Moran et al. found that only rings A and D are aromatic, thus, revealing the Clar structure of the
neutral circumcoronene. Since our ON values for $\pi$-electrons are less than 2.00 $|e|$, we performed an additional search adding six extra carbon atoms directly connected to a chosen hexagon. The results of the AdNDP analysis are shown in Fig. 6-5. One can see that a $\pi$-electron pair is completely delocalized over the 12 atoms though 92–94 % of its density is located over the hexagon.

In order to assess aromaticity of different rings (A, B, C, D) in these fragments we calculated NICS values and their zz-components ($\text{NICS}_{zz}$) as well as delocalization indices (DIs) [31, 32] which in a more general nomenclature are called electron sharing indices (ESIs). For this purpose we also calculated electronic multicenter indices (MCIs) [33], which, as has been recently shown, give excellent results for organic [34], all-metal [35], and inorganic [36, 37] aromatic clusters, providing aromaticity trends that are superior to those furnished by NICS.

We summarize calculated NICS and $\text{NICS}_{zz}$ data in Table 6-1. The calculated NICS and $\text{NICS}_{zz}$ values do not produce a coherent picture of aromaticity in our model systems. However, according to Poater et al., not only can the NICS indicator of aromaticity potentially incorporate spurious information arising from the electron flow perpendicular to the molecular plane, but also in addition paratropic (or diatropic) ring currents in adjacent rings can also produce a large effect on the NICS values of a ring [38]. The para-delocalization (PDI), fluctuation (FLU), MCI, $I_{\text{ring}}$ indices of the 1-19 rings (Fig. 6-6) are summarized in Tables 6-2–6-4. The calculated PDI, FLU, MCI and $I_{\text{ring}}$ indices support our local aromatic picture, since all indices indicate the presence of aromaticity in every ring.
Moreover, our local aromaticity chemical bonding picture in the studied model fragments of graphene is in concordance with the results of Matito and co-workers for the series of benzenoids macrocycles (C_{42}H_{18}, C_{78}H_{30}, C_{114}H_{30}, C_{186}H_{42}, C_{222}H_{42}, C_{258}H_{54}, C_{330}H_{54}) [39]. They showed that all the indices (PDI, FLU, MCI and I_{ring}) reproduce the same aromaticity for the central ring in the molecules with the number of outer rings exceeding five. They also showed that for such large benzenoid systems different rings become more and more equally aromatic with increasing number of outer rings. This supports our local aromaticity picture in the graphene lattice model fragments studied here.

6-3. Conclusions

Our results clearly show that graphene is aromatic, but its aromaticity is different from the aromaticity in benzene, coronene, or circumcoronene. The AdNDP analysis proved that graphene is locally aromatic with two π-electrons located over every hexagon ring and there is no global π-delocalization in graphene. The additional search revealed that a π-electron pair is completely delocalized over the 12 atoms although 92–94% of its density is located over the hexagon. We confirmed this by calculating PDI, FLU, MCI, and I_{ring} indices that show a local aromaticity picture for all the fragments studied. We believe that the chemical bonding picture derived here will be important for rationalizing different kinds of defects such as point defects, single-, double-, and multiple vacancies, carbon adatoms, foreign adatoms, substitutional impurities, and new materials that are derivatives of graphene.
6-4. Methods

Chemical bonding analysis of graphene model fragments was performed using the adaptive natural density partitioning (AdNDP) method recently developed by Zubarev and Boldyrev [24]. The AdNDP method analyzes the first-order reduced density matrix in order to obtain its local block eigenfunctions with optimal convergence properties for an electron density description. The obtained local blocks correspond to the sets of $n$ atoms ($n$ ranging from one to the total number of atoms in the molecule) that are tested for the presence of two-electron objects ($n$-center two electron ($nc-2e$) bonds, including core electrons and lone pairs as a special case of $n = 1$) associated with this particular set of $n$ atoms. AdNDP initially searches for core electron pairs and lone pairs ($1c-2e$), then $2c-2e$, $3c-2e$, ..., and finally $nc-2e$ bonds. At every step the density matrix is depleted of the density corresponding to the appropriate bonding elements. A user-directed form of the AdNDP analysis can be applied to specified molecular fragments and is analogous to the directed search option of the standard natural bond orbital (NBO) code [40, 41]. AdNDP accepts only those bonding elements, whose ON exceed the specified threshold values, which are usually chosen to be close to 2.00 $|e|$. When all recovered $nc-2e$ bonding elements are superimposed onto the molecular frame the overall pattern always corresponds to the point group symmetry of the system. Thus, the AdNDP method recovers both Lewis bonding elements ($1c-2e$ and $2c-2e$ objects, corresponding to the core electrons and lone pairs, and two-center two-electron bonds) and delocalized bonding elements, which are associated with the concepts of aromaticity and antiaromaticity. From this point of view, AdNDP achieves seamless description of systems featuring both localized and delocalized bonding without invoking the concept of
resonance. Essentially, AdNDP is a very efficient and visual approach to interpretation of the molecular orbital-based wave functions. We used a hybrid density functional method known in the literature as B3LYP [42–44] and the 6-31G basis set. The AdNDP calculations were performed using the AdNDP program written by Zubarev [24] and the Gaussian 03 software package [45]. Molecular visualization was performed using Molekel 5.4 [46].

We used the NICS [18] as well as its NICS$_{zz}$ [47] to assess aromaticity in our fragments. The use of NICS and NICS$_{zz}$ indices has been recently reviewed [48].

We also calculated DIs, which in a more general nomenclature are called ESIs, in order to assess the aromaticity of different rings in the graphene model fragments. Calculation of atomic overlap matrices and computation of ESI and MCI were performed with AIMPAC (theory of atoms in molecules) [49] and the ESI-3D [50] collection of programs at the B3LYP level of theory with the 6-311G** basis set for the C$_6$H$_6^{4+}$ and C$_{24}$H$_{12}^{10+}$ fragments and the 6-31G** basis set for the C$_{54}$H$_{18}^{16+}$ fragment. The numerical accuracy of the calculations was assessed by using two criteria: (1) the integration of the Laplacian of the electron density ($\nabla^2 (\rho)$) within an atomic basin must be close to zero, and (2) the number of electrons in a molecule must be equal to the sum of all the electron populations of the molecule and also to the sum of all the localization indices and half of the DIs in the molecule. For all atomic calculations, integrated absolute values of ($\nabla^2 (\rho)$) were always less than 0.001 a.u. For all the fragments, errors in the calculated number of electrons were always below 0.01 a.u.
References


[46] Varetto, U. *Molekel 5.4.0.8*, Swiss National Supercomputing Centre, Manno (Switzerland).


Tables and Figures

Table 6-1 Calculated NICS and NICS$_{ZZ}$ values (ppm) of rings at different z-coordinates for C$_6$H$_6$$^{4+}$, C$_{24}$H$_{12}$$^{10+}$ and C$_{54}$H$_{18}$$^{16+}$ fragments at the B3LYP/6-31G level of theory

<table>
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<tr>
<th>R$_a$ (Å)</th>
<th>C$_6$H$_6$$^{4+}$</th>
<th>C$<em>{24}$H$</em>{12}$$^{10+}$</th>
<th>C$<em>{54}$H$</em>{18}$$^{16+}$</th>
</tr>
</thead>
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<td>-15.86</td>
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<td>-1.39</td>
</tr>
<tr>
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<td>-7.86</td>
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<td>-1.41</td>
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</table>

$^a$ Distance from the hexagon center

$^b$ NICS$_{ZZ}$ values

Table 6-2 Electron delocalization and aromaticity indices for the C$_6$H$_6$$^{4+}$ fragment at the B3LYP/6-311G** level of theory

<p>| | | | |</p>
<table>
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</thead>
<tbody>
<tr>
<td>PDI</td>
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<td></td>
</tr>
<tr>
<td>PDI$_{\sigma}$</td>
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<td></td>
</tr>
<tr>
<td>PDI$_{\pi}$</td>
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<td></td>
</tr>
<tr>
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<td></td>
<td></td>
</tr>
<tr>
<td>MCI</td>
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<td>I$_{ring}$</td>
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Table 6-3 Electron delocalization and aromaticity indices for the C$_{24}$H$_{12}$$^{10+}$ fragment at the B3LYP/6-311G** level of theory

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<tr>
<td>MCI$_{\sigma}$</td>
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<tr>
<td>I$_{ring}$</td>
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Table 6-4  Electron delocalization and aromaticity indices for the C_{54}H_{18}^{16+} fragment at the B3LYP/6-31G** level of theory

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<th>PDI</th>
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<th>PDI_π</th>
<th>FLU</th>
<th>MCI</th>
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Figure 6-1 Molecular fragments of graphene selected for chemical bonding analysis

Figure 6-2 The C₆H₆⁺ structure, six 2c-2e C–C σ-bonds, six 2c-2e C–H σ-bonds superimposed on the fragment framework, and a 6c-2e π-bond. ON denotes the occupation number
**Figure 6-3** The \( \text{C}_{24}\text{H}_{12}^{10+} \) structure with 30 2c-2e C–C σ-bonds superimposed on the fragment framework, 12 2c-2e C–H σ-bonds superimposed on the fragment framework, and seven 6c-2e π-bonds

**Figure 6-4** The \( \text{C}_{54}\text{H}_{18}^{16+} \) structure, with 72 2c-2e C–C σ-bonds superimposed on the fragment framework, 18 2c-2e C–H σ-bonds superimposed on the fragment framework, and 19 6c-2e π-bonds
Figure 6-5 $\pi$-bonds recovered by the AdNDP analysis over six and 12 carbon atoms

Figure 6-6 Ring numbers in the $\text{C}_{54}\text{H}_{18}^{16+}$ fragment
CHAPTER 7

DECIPHERING CHEMICAL BONDING IN A BC\textsubscript{3} HONEYCOMB EPITAXIAL SHEET\textsuperscript{1}

Abstract

The substitution of every fourth carbon atom in graphene by a boron atom preserves the honeycomb structure in the BC\textsubscript{3} two-dimensional lattice, but as we found in our adaptive natural density partitioning analysis, it remarkably alters the chemical bonding. First, in the BC\textsubscript{3} lattice, where boron atoms are surrounded by three carbon atoms, carbon forces boron to form two-center–two-electron B–C $\sigma$-bonds, while boron is known to participate only in multicenter (three-center–two-electron or four-center–two-electron) $\sigma$-bonding in the most stable two-dimensional form of the pure boron lattice, the $\alpha$-sheet. Second, six-center–two-electron $\pi$-bonds found over every hexagon in graphene and in the $\alpha$-sheet migrate in BC\textsubscript{3} to hexagons composed of carbon atoms only, making $\pi$-bonding in those hexagons more similar to the corresponding $\pi$-bonding in benzene rather than graphene, leaving hexagons formed by carbon and boron atoms in the BC\textsubscript{3} lattice empty without $\pi$-bonding. We believe that chemical bonding elements found in our chemical bonding analysis of graphene, the $\alpha$-sheet of boron, and the BC\textsubscript{3} lattice will be useful tools for rationalizing chemical bonding in other two-dimensional boron–carbon materials.

7-1. Introduction

Pure boron\textsuperscript{1-4} and boron–carbon\textsuperscript{5-13} two-dimensional materials have gained significant attention since the discovery of graphene.\textsuperscript{14,15} The isolated layers of graphene were found to have many unusual properties such as high carrier mobilities (>200 000 cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1} at electron densities of 2 \times 10\textsuperscript{11} cm\textsuperscript{-2}),\textsuperscript{16-19} exceptional Young modulus values (>0.5–1 TPa), and large force constants (1–5 N m\textsuperscript{-1}).\textsuperscript{20-22} Due to these properties graphene is attractive for many potential commercial applications such as energy storage\textsuperscript{23} and micro- and optoelectronics.\textsuperscript{24} There is no doubt that other two-dimensional materials have a great potential for nanotechnology as much as graphene.

Understanding chemical bonding in these two-dimensional materials is crucial for rationalizing different kinds of defects such as point defects, single, double, and multiple vacancies, foreign adatoms, substitutional impurities,\textsuperscript{25} and new materials that are their derivatives. In our previous studies we analyzed chemical bonding in graphene\textsuperscript{26} and the most stable form of two-dimensional boron, the so-called \(\alpha\)-sheet.\textsuperscript{4} According to our analysis, \(\sigma\)-bonding in graphene is built out of two-center–two-electron (2c–2e) C–C \(\sigma\)-bonds, making the graphene honeycomb structure very rigid. The \(\pi\)-bonding in graphene is very different from the corresponding \(\pi\)-bonding in benzene, coronene, or other polycyclic hydrocarbons, because aromaticity in graphene is local with one pair of \(\pi\)-electrons located over every hexagon. The chemical bonding in the \(\alpha\)-sheet is also very different from that of graphene.

The \(\alpha\)-sheet structure is built out of filled and empty hexagons.\textsuperscript{1-3} According to our analysis, there are three 3c–2e \(\sigma\)-bonds in every filled hexagon which border the holes, three 4c–2e \(\sigma\)-bonds at the junction of two filled hexagons, one 7c–2e \(\pi\)-bond
delocalized over the filled hexagon, and one 6c−2e π-bond delocalized over the empty hexagon, so in total, there are eleven electrons participating in the formation of chemical bonding of the filled hexagon: six valence electrons coming from the three 3c−2e σ-bonds, three valence electrons coming from the three 4c−2e σ-bonds, and two electrons coming from the 7c−2e π-bond. On the other hand, the filled hexagon, considered as a part of the lattice, should have nine valence electrons coming from the six peripheral boron atoms and three valence electrons coming from the central atom, resulting in twelve electrons per filled hexagon. Thus, there is one extra electron on each filled hexagon motif not involved in the bonding presented above. This extra electron is involved in formation of the 6c−2e π-bond over the empty hexagons. Therefore, the α-sheet structure needs those empty hexagons as scavengers of extra electrons from the filled hexagons. In contrast to graphene, which contains 2c−2e C−C σ-bonds, the all-boron α-sheet possesses no localized 2c−2e B−B σ-bonds.

These two different chemical bonding pictures presented for graphene and the α-sheet raise the following question: What kind of chemical bonding can one expect in two-dimensional carbon–boron lattices? In this paper we present our analysis of chemical bonding in a BC₃ honeycomb sheet, based on the experimental structure presented in Figure 7-1, which was determined by low-energy electron diffraction.⁷

7-2. Theoretical Methods

Chemical bonding analysis of a BC₃ honeycomb sheet was performed using the fragmental approach and adaptive natural density partitioning (AdNDP) method recently developed by Zubarev and Boldyrev.²⁷ AdNDP initially searches for core electron pairs
and lone pairs (1c−2e), then 2c−2e, 3c−2e, ..., and finally nc−2e bonds if necessary. At every step the density matrix is depleted of the density corresponding to the appropriate bonding elements. The user-directed form of the AdNDP analysis can be applied to specified molecular fragments and is analogous to the directed search option of the standard natural bond orbital (NBO) code.28,29 AdNDP accepts only those bonding elements whose occupation numbers (ONs) exceed the specified threshold values, which are usually chosen to be close to 2.00 |e|. The AdNDP method recovers both Lewis bonding elements (1c−2e and 2c−2e objects, corresponding to the core electrons and lone pairs, and 2c−2e bonds) and delocalized bonding elements, which are associated with the concepts of aromaticity and antiaromaticity. We used a hybrid density functional method known in the literature as B3LYP30,31 and the 6-31G basis set32 for the AdNDP calculations. Geometry optimization and frequency calculations for the model fragments B_{6}C_{6}H_{12}, B_{10}C_{12}H_{18}, and B_{16}C_{24}H_{24} were performed using the B3LYP/cc-pvTZ33,34 level of theory. To assess the aromaticity of different rings in these fragments, we calculated nucleus independent chemical shift (NICS) indices.35,36 The AdNDP calculations were performed using the AdNDP program written by Zubarev.27 All density functional theory (DFT) calculations were done using the Gaussian 03 software package.37 Molecular visualization was performed using Molekel 5.4.0.8.38

7-3. Results and Discussion

Our first B_{6}C_{6}H_{12} fragment is shown in Figure 7-2 as structure II. This is the smallest fragment where we believe the chemical bonding in the infinite lattice is primarily preserved. Bonds between boron and carbon atoms in the extended honeycomb
sheet, shown in Figure 7-1, are substituted by B–H σ-bonds, which as we will see do not disturb much the chemical bonding in the fragment compared to the infinite sheet. Since our fragment is also a regular molecule, we performed geometry optimization and frequency calculations for structures I–III at the B3LYP/cc-pVTZ level of theory. Our fragment structure II is in fact a ninth-order saddle point. Geometry optimization following the imaginary frequencies led us to structure I, which is the most stable isomer found in our calculations. Even though structure II is not even a local minimum, we believe that it represents the correct chemical bonding pattern in the infinite BC$_3$ lattice. Our calculated $R$(C–C) = 1.43 Å bond and $R$(B–C) = 1.58 Å (at B3LYP/cc-pVTZ) are very close to the experimental values of $R$(C–C) = 1.42 Å and $R$(B–C) = 1.55 Å.$^7$ The optimized $R$(C–C) bond is about the same in all three structures, but the optimized $R$(B–C) bond varies from 1.52 to 1.58 Å. We also mention that structure II, which serves as the model fragment, is about 30 kcal/mol higher in energy than structure I, showing that the BC$_3$ lattice, presented in Figure 7-1, has some strain energy even though it was shown to be the most stable form for this stoichiometry.$^9$ We believe that the reason why structure II is not a minimum is the repulsion between terminal hydrogen atoms. To test that, we first optimized the geometries and calculated the frequencies of two molecules: 1,2-C$_6$H$_4$(BH$_2$)$_2$ and 1,3-C$_6$H$_4$(BH$_2$)$_2$. We found that both of these molecules are completely planar in the most stable configuration. Apparently, repulsion between just two H atoms is not enough to overcome stabilization due to conjugation of the π-system of C$_6$ with empty orbitals of boron. We next calculated 1,2,3-C$_6$H$_4$(BH$_2$)$_2$ and 1,3,5-C$_6$H$_4$(BH$_2$)$_2$. The 1,3,5-C$_6$H$_4$(BH$_2$)$_2$ molecule is most stable when it is completely planar, but in this case the BH$_2$ groups are well separated from each other. However, the
completely planar structure of the 1,2,3-C$_6$H$_4$(BH$_2$)$_2$ molecule has two imaginary frequencies. Thus, we proved that the repulsion between hydrogen atoms is responsible for the instability of isomer II in the C$_6$(BH$_2$)$_6$ case.

The results of the AdNDP analysis for the B$_6$C$_6$H$_{12}$ fragment are shown in Figure 7-3. Our analysis revealed six 2c−2e C−C σ-bonds, six 2c−2e B−C σ-bonds, and twelve 2c−2e B−H σ-bonds, which all have ON values that are close to the ideal value of 2.00 |e|. Thus, σ-bonding in this fragment between boron and carbon atoms as well as between carbon atoms is very similar to that of graphene in a sense that these bonds are 2c−2e. According to the AdNDP analysis, there are three 6c−2e π-bonds, which are very similar to those of benzene, which is not surprising since our fragment is a derivative of benzene. However, we point out that our ON values of π-bonds (1.75 and 1.89 |e|) in the fragment are appreciably lower than the ON values of π-bonds (2.00 |e|) in benzene. The deviation of the ON values of π-bonds from 2.00 |e| in this fragment indicates that these bonds tend to be delocalized over a larger number of atoms than six. Indeed, when we performed the direct search for the π-bonding on twelve atoms including both carbon and boron atoms, we obtained ON values of 2.00 |e| for all the π-bonds. Thus, the difference between 6c−2e and 12c−2e bonds is due to the participation of 2p$_z$ atomic orbitals (AOs) of boron in π-bonding, which turned out to be 0.10 |e| per boron atom. The degree of the participation of boron atoms in π-bonding can also be evaluated from the NBO analysis of structures II and III since delocalization of π-bonding toward boron atoms is possible in structure II, but not possible in structure III. According to our NBO analysis, we found that the boron atom in structure II has the higher occupation number of 2p$_z$ AOs by 0.06 |e| than the boron atom in structure III. This result is consistent with our AdNDP analysis.
Since our analysis and the B3LYP method both work well if the wave function is essentially one-configurational, we performed single-point CASSCF(14,15)/6-31G calculations. According to these results, the Hartree-Fock configuration has a 0.964 coefficient out of a total of 20,707,830 configurations, thus confirming that our wave function is primarily one-configurational and our analysis is valid.

Our second B_{10}C_{12}H_{18} fragment is presented in Figure 7-4. The second fragment allows us to see how two boron atoms are affected by two carbon hexagons at the junction. Optimized $R(B-C)$ and $R(C-C)$ were found to be 1.57 and 1.42–1.44 Å, respectively, which are in good agreement with the experimental data. The AdNDP analysis revealed that all $\sigma$-bonds are classical 2c–2e bonds with the ON very close to 2.00 $|e|$. We found a set of three $\pi$-bonds delocalized over every carbon hexagon with about the same ON as in the B_{6}C_{6}H_{12} fragment, which is also an indication of some participation of boron atoms in the $\pi$-bonding.

Results obtained at the CASSCF(10,10)/6-31G level of theory indicate that the wave function of this model fragment is also one-configurational: the first coefficient in the expansion of the wave function equals 0.926 (the total number of configurations is 31,878).

Our third B_{16}C_{24}H_{24} fragment is shown in Figure 7-5. The third fragment is essentially a tetramer of the first fragment, and it contains four carbon hexagons and two boron atoms at the center with the surrounding atoms, which they would have in the infinite BC_{3} lattice. The optimized $R(B-C)$ and $R(C-C)$ were found to be 1.56–1.58 and 1.41–1.43 Å, respectively, which are again in good agreement with the experimental data for the lattice. As in the first two fragments all $\sigma$-bonds are classical with the ON close to
2.00 \text{ |e|}. We found a set of three $\pi$-bonds delocalized over every carbon hexagon with about the same ON as in the B$_6$C$_6$H$_{12}$ fragment, which also is an indication of some participation of boron atoms in the $\pi$-bonding. To test the chemical bonding picture recovered by the AdNDP method, we also performed NBO analysis at the B3LYP/6-31G//B3LYP/cc-pVTZ level of theory for the three fragments. Results of this analysis are presented in Figure 7-6.

Like in the AdNDP, the NBO analysis revealed that $\sigma$-bonding is classical, with the ON values varying between 1.96 and 1.99 \text{ |e|}. As for the $\pi$-bonding, the NBO analysis produced one of the Kekulé structures with three alternate double C–C bonds in each carbon hexagon. Thus, the NBO analysis confirmed the presence of aromatic benzene-like carbon hexagons in all the studied fragments. The low ON values of these double bonds also indicate their tendency to be delocalized.

To investigate aromaticity further, we calculated NICS and NICS$_{zz}$ indices over all the hexagons labeled in Figures 7-4 and 7-5 as A, B, C, and D. NICS and NICS$_{zz}$ indices were calculated over the center of those hexagons at the $z$ coordinates from $z = 0.0$ Å to $z = 2.0$ Å with an interval of 0.5 Å. Results of these calculations are summarized in Table 7-1.

To have reference points, we also calculated NICS and NICS$_{zz}$ indices for the prototypical aromatic molecule benzene at the same level of theory. Results of these calculations are summarized in Table 7-2. Negative values of NICS and NICS$_{zz}$ indicate the presence of aromaticity, while positive ones show the presence of antiaromaticity.$^{35,36}$ No matter what indices, NICS or NICS$_{zz}$, we considered, we found for the B$_{10}$C$_{12}$H$_{18}$ and B$_{16}$C$_{24}$H$_{24}$ fragments that hexagons (B and D) composed of carbon atoms are aromatic.
while hexagons (A and C) composed of carbon and boron atoms are antiaromatic. As for the B₆C₆H₁₂ fragment, both NICS and NICS₂₂ indices also show an aromatic picture for the C₆ ring though the values of NICS and NICS₂₂ are somewhat lower than those in benzene. Thus, the overall chemical bonding picture revealed by the AdNDP, NBO, NICS, and NICS₂₂ analyses is consistent. The one-configurational nature of the fragment wave function was confirmed at the CASSCF(8,8)/6-31G level of theory: the first coefficient in the expansion of the wave function is found to be 0.929 (the total number of configurations is 1764).

7-4. Conclusion

The chemical bonding analysis performed for the BC₃ lattice revealed a chemical bonding picture very different from the corresponding one in graphene and the all-boron α-sheet. We found that the σ-bonding in BC₃ is classical, composed of 2c−2e B−C and C−C bonds, reminiscent of that in graphene. Thus, carbon forces boron to form 2c−2e σ-bonds, in contrast with an all-boron α-sheet, where boron participates only in multicenter (3c−2e or 4c−2e) σ-bonding. However, in contrast with graphene, where there is one 6c−2e π-bond located over every hexagon, in the BC₃ lattice we have six π-electrons located over every carbon hexagon and there are no π-bonds over the hexagons, which are composed of boron and carbon atoms. Moreover, NICS and NICS₂₂ values indicate the presence of antiaromaticity in those hexagons. Thus, 6c−2e π-bonds found over every hexagon in graphene and in the α-sheet migrate to hexagons composed of carbon atoms only, making π-bonding in those hexagons more similar to the corresponding π-bonding in benzene rather then graphene, leaving hexagons formed by carbon and boron atoms in
the BC₃ lattice empty without π-bonding. The presence of boron atoms does not destroy the honeycomb network of σ-bonds in BC₃, while in a pure boron α-sheet there are no 2c−2e B−B σ-bonds. So far, analyzing the chemical bonding in two-dimensional boron, carbon, and boron–carbon materials, we found the following chemical bonding elements: 2c−2e C−C and B−C σ-bonds, 3c−2e σ-bonds and 4c−2e all-boron σ-bonds, 6c−2e all-carbon and all-boron π-bonds, 7c−2e all-boron π-bonds, and benzene-like π-bonding with six π-electrons located over the all-carbon hexagons. The one-configurational nature of the wave functions of all the fragments studied here is confirmed using the multiconfigurational method CASSCF. We strongly believe that these bonding elements will be important for rationalizing chemical bonding in other boron–carbon two-dimensional materials.

References


(38) Varetto, U. Molekel 5.4.0.8, Swiss National Supercomputing Centre, Manno (Switzerland).

### Tables and Figures

**Table 7-1.** Calculated NICS and NICS$_{zz}$ Values (ppm) at Different $z$ Coordinates for B$_6$C$_6$H$_{12}$, B$_{10}$C$_{12}$H$_{18}$, and B$_{16}$C$_{24}$H$_{24}$ Fragments at the B3LYP/cc-pVTZ//B3LYP/cc-pVTZ Level of Theory

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*Distance from the hexagon center. $^b$NICS$_{zz}$ values.

**Table 7-2.** Calculated NICS and NICS$_{zz}$ Values (ppm) at Different $z$ Coordinates For C$_6$H$_6$ at the B3LYP/cc-pVTZ//B3LYP/cc-pVTZ Level of Theory

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<th>NICS$_{zz}$</th>
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</tr>
<tr>
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<td>-17.46</td>
</tr>
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</table>

*Distance from the hexagon center. $^b$NICS$_{zz}$ values.
Figure 7-1. Atomic arrangement in the layer of BC$_3$. The green atom is B, and the brown atom is C.

Figure 7-2. B$_6$C$_6$H$_{12}$ molecular structures. The green atom is B, the brown atom is C, and the blue atom is H.
Figure 7-3. Chemical bonds revealed by the AdNDP analysis at B3LYP/6-31G//B3LYP/cc-pVTZ.

Figure 7-4. Structure and chemical bonds of the B$_{10}$C$_{12}$H$_{18}$ fragment revealed by the AdNDP analysis at B3LYP/6-31G//B3LYP/cc-pVTZ.
Figure 7-5. Structure and chemical bonds of the $\text{B}_{16}\text{C}_{24}\text{H}_{24}$ fragment revealed by the AdNDP analysis at B3LYP/6-31G//B3LYP/cc-pVTZ.
Figure 7-6. Kekulé structures for the $B_6C_6H_{12}$, $B_{10}C_{12}H_{18}$, and $B_{16}C_{24}H_{24}$ fragments found by the NBO analysis.
CHAPTER 8
TWO-DIMENSIONAL Cu₂Si MONOLAYER WITH PLANAR HEXACOORDINATE COPPER AND SILICON BONDING

Abstract

Two-dimensional (2D) materials with planar hypercoordinate motifs are extremely rare due to the difficulty in stabilizing the planar hypercoordinate configurations in extended systems. Furthermore, such exotic motifs are often unstable. We predict a novel Cu₂Si 2D monolayer featuring planar hexacoordinate copper and planar hexacoordinate silicon. This is a global minimum in 2D space, which displays reduced dimensionality and rule-breaking chemical bonding. This system has been studied with density functional theory, including molecular dynamics simulations and electronic structure calculations. Bond order analysis and partitioning reveals 4c−2e σ bonds that stabilize the two-dimensional structure. We find that the system is quite stable during short annealing simulations up to 900 K, and predict that it is a nonmagnetic metal. This work opens up a new branch of hypercoordinate two-dimensional materials for study.

8-1. Introduction

Since the isolation and characterization of graphene,¹ the field of two-dimensional (2D) materials has attracted tremendous attention² and has evolved into a huge family of

new exciting materials. This diverse group of 2D materials includes boron nitride,\textsuperscript{3,4} dichalcogenide,\textsuperscript{3,5} tertiary B–C–N,\textsuperscript{6} and group IV,\textsuperscript{7–11} II–VI,\textsuperscript{12–14} and III–V\textsuperscript{15–17} compounds. The ensuing impact on physics, materials science, and chemistry has been broad, including many fundamental and ingenious discoveries.

Considering these 2D materials from the viewpoint of structural and coordination chemistry, most have tricoordinated motifs, as demonstrated by graphene.\textsuperscript{18} Only a few examples of (quasi)-planar tetracoordinated configurations have been reported; the first planar tetracoordinated carbon motifs in 2D networks based on C\textsubscript{5}\textsuperscript{2–} were reported by Hoffmann et al.\textsuperscript{19} followed by studies of B\textsubscript{4}C\textsubscript{2},\textsuperscript{20} SiC\textsubscript{2},\textsuperscript{21} TiC,\textsuperscript{22} and Al\textsubscript{4}C.\textsuperscript{23} Planar hexacoordinated motifs, first conceived by Schleyer and Exner in isolated molecules,\textsuperscript{24} are extremely rare in 2D materials. Planar hexacoordinated 2D boron sheets have been proposed theoretically\textsuperscript{25–30} and boron nanoclusters have been observed spectroscopically.\textsuperscript{31,32} It has been very challenging to create planar hypercoordinate 2D materials, as one needs to match the constituent elements both geometrically and electronically. In 2014, Schleyer and co-workers reviewed the history and progress in the prediction and fabrication of planar hypercoordinate molecules and extended systems.\textsuperscript{33} In terms of fundamental science and potential applications, 2D hypercoordination materials are very exciting and attractive.

Recently, a Be\textsubscript{2}C monolayer featuring quasi-planar hexacoordinate carbon (phC) has been proposed.\textsuperscript{34} However, this material has a 0.46 Å vertical corrugation out of the plane. The theoretically predicted one-dimensional \((\text{SF}_4\text{–SF}_4)_\infty^–\) species with hexacoordinated sulfur atoms exhibiting direct S–S bonds await experimental confirmation.\textsuperscript{35}
In this paper, on the basis of comprehensive density functional theory (DFT) computations, we predict a new completely flat 2D hexacoordinated structure. This is a 6-fold symmetric Cu$_2$Si monolayer with each Si atom coordinated with six Cu atoms to form a planar hexacoordinate silicon (phSi) structure. At the same time, each Cu is coordinated with three Si atoms and three Cu atoms to form a planar hexacoordinate copper (phCu) structure. These phSi and phCu elements are alternatively arranged to form an infinite sheet as shown in Figure 8-1a. This material is the first example of a simultaneously phSi and phCu-containing material. Our DFT computations demonstrate that this Cu$_2$Si monolayer has excellent stability. It is the global minimum structure in the 2D space, and so has promise for experimental synthesis.

8-2. Computational methodologies

The electronic structure and total energy were calculated using DFT via the plane-wave pseudopotential (PWPP) technique implemented in the Vienna ab initio simulation package (VASP). The projector-augmented wave (PAW) method was used to represent the ion–electron interaction. The generalized gradient approximation (GGA) expressed by the PBE functional, and a 500 eV cutoff for the plane-wave basis set were adopted in all calculations. The convergence threshold was set as $10^{-6}$ eV in energy and $10^{-3}$ eV/Å in force. We placed the monolayer Cu$_2$Si sheet in the $xy$ plane with the $z$ direction perpendicular to the layer plane. A vacuum space of 15 Å in the $z$ direction was used to avoid interactions between adjacent layers. The Brillouin zone was sampled with a $12 \times 12 \times 1$ $\Gamma$-centered Monkhorst–Pack (MP) K-points grid. Phonon dispersion was calculated using density-functional perturbation theory (DFPT), as implemented in the
Quantum-ESPRESSO package. This was done within the local-density approximation (LDA) and using PAW pseudopotentials. Cutoffs of 80 and 1000 Ry were used for wave functions and charge density, respectively. The Brillouin zone was sampled with a $32 \times 32 \times 1$ Monkhorst–Pack (MP) grid, and dynamical matrices were calculated on a $12 \times 12 \times 1$ MP grid. For the deformation charge density, the electronic configuration used for Cu is $3d^{10}4s^1$ and for Si is $3s^23p^2$.

Born–Oppenheimer molecular dynamics (BOMD) simulations were performed to assess the thermal stability of the Cu$_2$Si monolayer. The DSPP pseudopotential and GGA PBE functional were used, as implemented in Dmol$^3$ software in Materials Studio 7.0. MD simulations in the NVT ensemble were carried out for 3–10 ps with a time step of 1.0 fs (parameters: accuracy fine, DND, DFT-D TS, SCF $= 2 \times 10^{-6}$, smearing $= 0.01$, DIIS $= 10$, Nose-Hoover, Nose Q $= 2$, Nose chain length $= 2$). Due to limitations of the program, no warmup period was used. For the MD simulations, a $4 \times 4$ supercell was used in a $12.5 \times 16.5 \times 12$ Å$^3$ box. The temperature was controlled using the Nosé–Hoover method. Materials studio was also used to create the initial structures and visualize the results.

The crystal structure predictions were performed with particle-swarm optimization (PSO) method as implemented in the CALYPSO code. The PSO algorithm offers an efficient and fast way to obtain reliable structures with only the input of chemical composition. The algorithm searches for structures with space group symmetry.

In our PSO simulation, the population size and the number of generation were set to be 30. The number of formula units per simulation cell was set as 1 to 6; that is, unit cells containing total number atoms of 3, 6, 9, 12, 15, and 18 were considered. The
structure relaxations during the PSO simulation were performed using the PBE functional as implemented in VASP. High-quality renderings of the molecular structures were produced with the UCSF Chimera package.

The same parameters were used for the periodic NBO and SSAdNDP calculations as for the VASP calculations. Similar to standard NBO code, periodic NBO allows determination of Lewis elements of localized bonding, such as 1c−2e bonds (lone pairs) and 2c−2e bonds (classical two-center two-electron bonds), whereas SSAdNDP enables delocalized bonding (nc-2e bonds, n > 2) to be found in addition. The SSAdNDP projection algorithm was used to obtain a representation of the delocalized plane wave DFT results in a localized atomic orbital basis. As long as an appropriate atomic orbital basis set is chosen (it is usually trimmed of any functions with angular momentum \( l \geq 4 \) as well as diffuse functions with exponents < 0.1), projection is found to result in an accurate density matrix. For the 2D Cu₂Si system, the Def2-SV(P) basis set was used to represent the projected PW density using a \( 7 \times 7 \times 3 \) k-point grid. This basis set was selected so that on average less than 1% of the density of each occupied plane wave band was lost in projecting into the AO basis to guarantee that the density matrix used in the SSAdNDP procedure accurately represents the original plane wave results. The Visualization for Electronic and Structural Analysis software (VESTA, series 3) was used for visualization of the SSAdNDP results.

8-3. Results and discussion

The ground state structure of Cu₂Si was obtained using a comprehensive particle swarm structural search with CALYPSO code followed by the full relaxation of random
structures with VASP\textsuperscript{36}. Having located the global minimum structure of the Cu\textsubscript{2}Si monolayer (Figure 8-1a), we then performed an analysis of properties including chemical bonding, cohesive energy, mechanical properties, dynamic stability, thermal stability, and electronic properties.

To evaluate the chemical bonding of the phSi and phCu atoms, we computed the deformation electronic density. This quantity is defined as the total electronic density of the Cu\textsubscript{2}Si monolayer minus the electron density of isolated Cu and Si atoms at their respective positions. Thus, the deformation density is well suited to probe the valence electron delocalization. Indeed, Figure 8-1b shows a smooth, delocalized electron deformation density, as one would expect for a metal, with holes in the deformation electron density near the atomic positions (due to the pseudopotentials). The Hirshfeld charge analysis (from Dmol\textsuperscript{3} calculations) shows that each Cu atom transfers 0.06 e to each Si atom.

To understand the unique chemical bonding in Cu\textsubscript{2}Si monolayer, we have utilized periodic natural bond orbital (NBO)\textsuperscript{52} analysis. In total, there are 22 valence electrons from two Cu atoms and four valence electrons from each Si atom per unit cell. This analysis found ten $d$-type lone pairs on the two Cu atoms (five on each atom) with occupation number of $1.9\sim 2.0\ |e|$ (see Figure 8-2).

We have also used an extension of the periodic natural bond orbital method, the Solid State Adaptive Natural Density Partitioning (SSAdNDP)\textsuperscript{53} method. It is noteworthy that both methods have shown the absence of any classical two-center two-electron (2c–2e) $\sigma$ bonds. The SSAdNDP analysis identifies both localized (nc–2e bonds, n$\leq$2) and delocalized (nc–2e bonds, n>$2$) bonding elements in the Cu\textsubscript{2}Si monolayer. It found the
same 10 lone pairs on two Cu atoms with occupation number 1.9–2.0 |e| as well as three 4c−2e σ bonds with occupation number 1.9 |e|, thus accounting for 26 electrons per unit cell. These 4c−2e σ bonds are shown in Figure 8-3a–c. Thus, one can see that the delocalized bonding governs the planar geometry of the Cu₂Si sheet. This chemical bonding picture is consistent with the symmetry of the 2D crystal. We observe that the deformation charge density of Figure 8-1b is similar to the superposition of 4c−2e σ bonds shown in Figure 8-3d.

The calculated Si−Cu and Cu−Cu bond lengths are both close to 2.38 Å. One unit cell of the Cu₂Si monolayer consists of two Cu atoms and one Si atom, with optimized lattice constants of $a = b = 4.123$ Å. The band structure indicates the material is metallic with a large density-of-states (DOS) at the Fermi level. The Cu₂Si monolayer is diamagnetic as confirmed by a spin-polarized computation, indicating that the compound has a nonmagnetic ground state and there are no unpaired electrons or unsaturated dangling bonds.

To evaluate the stability of this structure, we first computed the cohesive energy $E_{\text{coh}} = (xE_{\text{Si}} + 2xE_{\text{Cu}} - xE_{\text{Cu}_2\text{Si}})/3x$, with $E_{\text{Cu}}$, $E_{\text{Si}}$, and $E_{\text{Cu}_2\text{Si}}$ being the total energies of a single Cu atom, a single Si atom, and one unit cell of the Cu₂Si monolayer. The Cu₂Si monolayer has a cohesive energy of 3.46 eV/atom. For comparison, using the same computational method, the cohesive energies of graphene, silicene, and germanene are 7.85, 3.98, and 3.26 eV/atom, respectively. Thus, while the cohesive energy is significantly lower than that of the Cu and Si 3D bulk phases, it is sufficient when restricting the material to 2D, indicated by the stronger binding energy compared to germanene, and comparable to that of silicene.
The mechanical properties are important for potential application of the Cu$_2$Si material. The in-plane Young modulus, (or in-plane stiffness), is commonly used to evaluate the mechanical stability of 2D layered materials. We compare the calculated value of our new material to reported experimental values$^{54}$ and previous theoretical results$^{55,56}$ for several commonly known 2D materials, including graphene, MoS$_2$, germanene, and silicene. For the Cu$_2$Si monolayer, the in-plane stiffness was computed to be 93 N/m, which is lower than that of graphene (295 N/m). However, it is comparable to the in-plane stiffness of the MoS$_2$ monolayer (124 N/m), and higher than germanene (42 N/m) and silicene (61 N/m) computed at the same theoretical levels. Thus, the Cu$_2$Si monolayer shows strong mechanical stability.

The dynamical stability of the Cu$_2$Si monolayer was tested by calculating the phonon dispersion along the high-symmetry lines (Figure 8-4). All the frequencies are real, indicating its kinetic stability. No imaginary phonon modes are found in the whole Brillouin zone. In particular, the highest frequency reaches up to 420 cm$^{-1}$, indicating robust Cu–Si interaction. The lowest optical mode (90 cm$^{-1}$) corresponds to out-of-plane vibration of Cu atoms, while the highest, doubly degenerate, optical mode (390 cm$^{-1}$) corresponds to in-plane vibrations of Cu and Si atoms.

To verify that this new material will be stable at ambient conditions, we have performed Born–Oppenheimer molecular dynamics simulations. A 4 × 4 supercell was used in the MD simulations. A series of individual MD simulations were carried out to evaluate the thermal stability of the monolayer Cu$_2$Si material at temperatures of 300, 600, 900, 1200, and 1500 K (of duration 3, 4, 10, 10, and 4 ps respectively). Snapshots taken at the end of each simulation are shown in Figure 8-5. From the snapshots, one can see
that the planar hexacoordinate motifs were generally well-kept. The structure survives a 10 ps anneal up to 900 K. A survey of bond lengths shows individual bond lengths increasing temporarily by up to 16% at 900 K in the last 1 ps of the simulation, although most bonds stay shorter most of the time. Looking at the final 900 K snapshot in Figure 8-5, the system is still holding together well. At 1200 K, by 10 ps, the system is clearly starting to melt. The atoms are fluctuating significantly, and a survey of bond lengths shows individual bond lengths increasing temporarily by up to 37% at 1200 K. At 1500 K, the structure is seriously disrupted already after only 4 ps, and atoms have already started to exchange positions. The above results reveal that the Cu$_2$Si monolayer has very good thermal stability and can maintain its structural integrity during brief annealing up to 900 K.

After confirming that Cu$_2$Si monolayer is a stable local minimum structure, we show that this monolayer is actually a global minimum in 2D space. To address this issue, we have performed a global minimum search for the lowest-energy structure for Cu$_2$Si in the 2D space using first-principles based particle swarm optimization.$^{46}$ After a comprehensive structural search, the hexacoordinate Cu$_2$Si layer discussed above with uniform and highly symmetrical distribution of Si and Cu atoms was found to be the lowest energy structure in the 2D space. The three lowest stable planar hexacoordinate structures for 2D Cu$_2$Si with different patterns and relative distributions of Cu and Si atoms in the plane are shown in Figure 8-6. These three structures are low-lying isomers featuring planar hexacoordinate configurations with relative energies of 80, 121, and 160 meV/atom, respectively.
As a result of the search, we also found some planar tetracoordinate motifs for the Cu$_2$Si sheet. These structures also have very interesting structural properties: each Si atom binds to four Cu atoms in the same plane to form a ptSi moiety. However, their total energies are significantly higher than those of the four planar hexacoordinate motifs.

We have also considered buckled structures of 2D Cu$_2$Si, though all of them were found to be higher in energy than the planar hexacoordinate motifs. Therefore, the phSi/phCu containing Cu$_2$Si monolayer is the global minimum structure in the 2D space. This result is very exciting because the Cu$_2$Si monolayer is the first extended planar hexacoordinate Si containing structure. Previously, phSi motifs have only been rarely predicted computationally in isolated molecules such as SiCu$_6$H$_6$\textsuperscript{57} and SiB$_4$Si$_2$\textsuperscript{58}. We do not know whether these two molecules are global minima, and there has not been any follow-up experimental confirmation. Moreover, Cu atoms in the Cu$_2$Si monolayer are also in a planar hexacoordinate configuration. To our knowledge, there is no report to date of planar hexacoordinate Cu motifs, either on isolated molecules or in periodic structures. Since the phSi/phCu-containing Cu$_2$Si monolayer is the global minimum structure in 2D space, it holds great potential to be realized experimentally.

To get insight into electronic properties, we have computed the band structure as well as its density of states (DOS). As shown in Figure 8-7, the material shows a band structure typical for metals. The metallic character of Cu$_2$Si is demonstrated by the Fermi level (E = 0) being located inside the bands, and no observation of a band gap at this energy. Therefore, unlike semimetallic graphene, the Cu$_2$Si monolayer is a diamagnetic metal.
The projected density of states (PDOS) analysis shows that below the Fermi energy the major contribution comes from Cu-3d-states. The states at the Fermi level are dominated by the Si-3p, Cu-4p and Cu-3d states, with Si-3p more pronounced than Cu-4p and -3d. There is apparent hybridization between Si 3p- and Cu 4p-, 3d-states. This is consistent with the chemical bonding analysis of the Cu$_2$Si monolayer.

8-4. Conclusions

In summary, we have designed a new stable planar hexacoordinate 2D Cu$_2$Si monolayer. This material is metallic. In the Cu$_2$Si monolayer, each Si atom is coordinated to six Cu atoms to form a phSi moiety. Furthermore, each Cu atom is coordinated to three Cu and three Si atoms to form a phCu configuration. Chemical bonding analysis shows that multicenter $\sigma$ bonds stabilize the two-dimensional structure. The Cu$_2$Si monolayer has strong chemical bonding and high inplane stiffness. Local structural stability is predicted by the absence of any imaginary phonon modes. Molecular dynamics simulations show that this material is stable during short annealing runs up to 900 K. A Particle Swarm search confirmed that the Cu$_2$Si monolayer is the global minimum structure in 2D space. Considering the rapid development of experimental techniques for fabrication of low-dimensional materials in recent years, we are optimistic that the Cu$_2$Si monolayer can be fabricated experimentally in the near future.

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Figures

Figure 8-1. (a) Top and side views of the ball and stick model of the 2D Cu$_2$Si monolayer. 4 × 4 section of extended monolayer and (b) deformation charge density of the 2D Cu$_2$Si monolayer. Blue refers to electron accumulation. Copper atoms are brown, and silicon is gray.

Figure 8-2. Bonding structure of the Cu$_2$Si monolayer: five $d$-type lone pairs on one Cu atom.
Figure 8-3. Bonding structure of the Cu$_2$Si monolayer: (a–c) individual 4c-2e $\sigma$ bonds and (d) superposition of 4c-2e $\sigma$ bonds. Copper is orange, and silicon is blue.

Figure 8-4. Phonon dispersion and phonon density of states of the monolayer Cu$_2$Si sheet. $\Gamma$ (0, 0, 0), M (0, 1/2, 0), and K (1/3, 2/3, 0) refer to special points in the first Brillouin zone in reciprocal space.
Figure 8-5. Snapshots of the final frame of each molecular dynamics simulation from 300 to 1500 K (top and side views). Bonds to atoms outside this $4 \times 4$ section exist but are not shown.

Figure 8-6. Low lying isomers found by particle swarm search. Copper atoms are brown, and silicon is gray. Bonds to atoms outside of these sections exist but are not shown.
Figure 8-7. Electronic structure of Cu₂Si monolayer: band structure (left), total density of states (DOS) (middle), and projected density of states (PDOS) (right). The Fermi level is at 0 eV.
CHAPTER 9
THE I=\textit{X} (\textit{X} = \textit{O}, \textit{N}, \textit{C}) DOUBLE BOND IN HYPERVALENT IODINE COMPOUNDS: IS IT REAL?\(^1\)

Abstract

\textit{I=\textit{X}} (\textit{X} = \textit{O}, \textit{N}, \textit{C}) bonding was analyzed in the related hypervalent iodine compounds based on adaptive natural density partitioning (AdNDP) approach. The results confirm the presence of \textit{I}→\textit{X} \(\sigma\) dative bond, as opposed to the widely used \textit{I}=\textit{X} notation. A clear formulation of the electronic structure of these hypervalent iodine compounds would be useful in establishing reaction mechanisms and electronic structures in bioinorganic problems of general applicability.

Organic derivatives of polyvalent iodine, commonly known as hypervalent iodine reagents, have found widespread application in organic synthesis as versatile, efficient, and environmentally sustainable reagents.\(^{[1]}\) Despite extensive practical interest in these compounds, a relatively small number of computational studies on structure and reactivity of polyvalent iodine compounds have been published.\(^{[2]}\) In particular, an important question about the existence of \textit{I}=\textit{X} (\textit{X} = \textit{O}, \textit{N}, \textit{C}) double bonds in organic derivatives of trivalent and pentavalent iodine has not been reliably answered. Structures of key hypervalent iodine reagents, such as iodosylarenes (1), iodonium imides (2), iodonium ylides (3), iodylarenes (4), 2-iodoxybenzoic acid (IBX, 5), are commonly

shown in the original research papers, books, and reviews in the form of compounds with a double bond at the iodine atom (Figure 9-1).[1,2]

X-ray structural studies of these compounds in the solid state are inconclusive because the real molecular structure of hypervalent iodine derivatives is masked by extensive networks of intermolecular secondary bonds resulting in a highly aggregated polymeric structure.[3] For example, X-ray powder diffraction and EXAFS studies of iodosylbenzene have indicated a zigzag polymeric chain structure (6) in which monomeric PhIO units are linked by intermolecular I···O secondary bonds.[3a] In spite of the numerous experimental structural studies of hypervalent iodine compounds,[1] the question about the real nature of the I=X bonding remains open. Bonding description in such molecules is very important for understanding the structural, physical, and chemical properties. In the current study we show the single dative [two-center two-electron (2c-2e) bond where two electrons derive from the same atom] character of chemical bonding between I and O, I and N, and I and C atoms in hypervalent iodine compounds, and it is controversial with respect to the common I=X double-bond representation.

To establish a reliable picture of the chemical bonding we have probed various hypervalent iodine molecules, such as IO\textsuperscript{−}, PhIO, PhIO\textsubscript{2}, PhIO\textsubscript{3}, PhINR (R = SO\textsubscript{2}Ph), and PhICR\textsubscript{2} (R = CO\textsubscript{2}Me). The geometries of all the structures were optimized at the PBE0/I/Stuttgart/H, C, N, O, S/aug-cc-pVTZ\textsuperscript{[4-8]} level of theory with follow-up frequency calculations. All the structures were checked to be true minima with no imaginary frequencies. Chemical bonding analysis was performed using the adaptive natural density partitioning (AdNDP) method, which achieves a seamless description of systems featuring both localized and delocalized bonding without invoking the concept of
resonance. The AdNDP approach has demonstrated effectiveness in the description of chemical bonding in many organic, inorganic systems, and clusters.

It is known that the metaperiodate anion is composed of one iodine and four oxygen atoms, and is generally represented by having three double bonds between I and O, and one single I−O σ bond with a negative charge on the oxygen atom (Figure 9-2a). Application of the AdNDP method for the metaperiodate anion leads to the chemical bonding pattern shown in Figure 9-2.

AdNDP recovered one s-type and two p-type electron lone pairs (1c-2e) on each oxygen atom with occupation numbers (ONs) in the range of 1.84–1.99 |e|. Four 2c-2e I−O σ bonds (ON = 2.00 |e|) originate from the donation of electron density directly from iodine, thus indicating the dative character of these bonds. In addition, NBO analysis was performed to determine a charge distribution in this species. According to it, every oxygen atom bears a negative charge of −1.14, while iodine is positively charged (+3.56). Thus, our analysis shows that single dative I:→O bonds should be used to describe chemical bonding in IO₄⁻. The appropriate symbolic representation according to the AdNDP analysis is demonstrated in Figure 9-2b.

Iodosylbenzene was first synthesized by C. Willgerodt from iodobenzene in 1892 and it has the empirical formula PhIO. Similar to the IO₄⁻ case, it has been described as having a I=O bond (structure 1, Figure 9-1), a formulation which clearly breaks the octet rule at iodine. The results of the AdNDP analysis and the corresponding symbolic representation of PhIO are summarized in Figure 9-3. As expected, AdNDP revealed three lone pairs (ON=1.75–1.99 |e|) on the oxygen atom, one dative 2c-2e I→O σ bond with ON=2.00 |e|. The bonding between iodine and the carbon atom of the Ph group
derives from the sharing of an electron pair between these atoms and thus represents a common single covalent I–C σ bond (ON=1.97 |e|). The remaining electrons of I form two lone pairs with ON=1.99 |e| as shown in Figure 9-3. Complete AdNDP analysis of PhIO is given in Figure 9-6. We obtained a similar bonding pattern for PhIO₂ (see Figure 10-7) and PhIO₃ (see Figure 9-8), where the bonding between the iodine and oxygen atoms represents a single dative 2c-2e I→O σ bond and confirms the absence of I=O bonds. The situation described here appears to be akin to other oxyanions, including the well-known sulfate, nitrate, and phosphate anions (all of which we do not represent with a double-bond symbol) with an oxygen atom accepting the dative bond.

More complicated cases where the nature of the I–X bonding remains contentious were investigated using an iodonium imide and iodonium ylide (structures 2 and 3; Figure 9-1). Results of the AdNDP analyses on I–N and I–C fragments and nearby atoms are shown in Figure 9-4 and Figure 9-5, respectively.

As one can see, in the iodonium imide PhINR (R=SO₂Ph) there are two lone pairs on N with ON=1.84–1.97 |e| and two lone pairs on I with ON=1.97–1.99|e| (Figure 9-4). Covalent bonds at the studied fragments are represented by 2c-2e I–C and 2c-2e N–S σ bonds with ON=1.91 |e| and ON=1.96 |e|, respectively. Again, the bonding between I and N has a dative character and is represented by the single 2c-2e I→N σ bond according to our analysis. The chemical bonding picture of the iodonium ylide PhICR₂ (R=CO₂Me) shows one dative I→C σ bond (ON=1.96 |e|), one 2c-2e bond between I and C of the Ph fragment with ON=1.97 |e|, two lone pairs on I (ON=1.96–1.99 |e|), two 2c-2e C–C σ bonds (ON=1.98 |e|), and one 3c-2e π bond (ON=1.80 |e|) delocalized over three carbon atoms (Figure 9-5).
The 3c-2e π bond is responsible for the bending of the C-C-C fragment and can actually be represented by a lone pair on the central carbon atom with a somewhat lower occupation number (ON=1.48 |e|). This data is supported by the NBO analysis, thus showing a positive charge of +0.75 on two flanking carbon atoms and a negative charge of −0.58 on the central carbon atom. The need to form the 3c-2e π bond comes from the fact that the carbon atom is less electronegative than either N or O and needs some help from its neighboring carbon atoms, thus transforming a lone pair into the 3c-2e π bond. The presence of this 3c-2e π bond seems to explain the C−C bond length (1.44 Å) on this fragment, which is something average between the single and double C−C bond lengths. Similar cases wherein a 3c-2e π bond originates from the lone pair on the central carbon atom and makes the corresponding C−C distances shorter than a typical C−C bond length, are exemplified by such molecules as C₈B₂⁻, C₉B⁻, and C₁₀⁻.\[10g\]

The bonding picture developed for PhIC(CO₂Me)₂ through the AdNDP analysis shows that the single dative I→C σ bond can be formed only if electron-withdrawing groups like CO₂Me take some electron density from the carbon atom (its charge is not −1.0 but only −0.58) connected to the iodine atom because the carbon atom is not electronegative enough to acquire two electrons from the iodine atom alone.

Essentially, the studied iodine compounds can be described as Lewis bases bonded to Lewis acids [-O, -NSO₂Ph, and -C(CO₂Me)₂]. This description means that the Lewis acidity of the three latter species should be related to the strength of the bonding to the iodine-containing Lewis base. Hence, the strength of donor–acceptor interactions would be defined by the Lewis basicity/acidity of the components. The computed interaction energies between donor (PhI⁻) and corresponding acceptors suggest that -O
(−211.4 kcal mol⁻¹) is a stronger Lewis acid than -NSO₂Ph (−132.0 kcal mol⁻¹) and -C(CO₂Me)₂ (−163.6 kcal mol⁻¹) and that the strength of the donor–acceptor bonds follows the trend for the acceptors: O>C(CO₂Me)₂>NSO₂Ph. Thus, we believe that the derived description of the presented hypervalent iodine compounds as donor–acceptor complexes might be a very useful model for classifying known iodine compounds as well as for the design and prediction of novel molecules where the Lewis base and/or the Lewis acid are changed. Furthermore, our results might also be relevant to a broader range of existing compounds such as the carbodiphosphorane Ph₃P=C=PPh₃,[14] the borylene complex (BH)L₂,[15] the silylones SiL₂,[16] as well as the germylonones GeL₂[17] (with different N-heterocyclic carbenes as ligands L), where a single dative bond rather than the double-bond character was confirmed based on their electronic structures and chemical behavior.[18-21]

According to the obtained chemical bonding pictures of all the studied molecules, it is clearly seen that the octet rule is obeyed in each case. Although we have used the term hypervalent throughout our discussion, it is noteworthy that it was purposely used to describe molecules which contain elements in any of their oxidation states other than their lowest oxidation state, and is in concordance with Musher’s definition of a hypervalent molecule.[22] However, we agree with Gillespie and Silvi[23] who concluded that hypervalence is not a useful concept as hypervalent molecules are not different in any significant way from Lewis octet molecules.

In conclusion, we performed chemical-bonding analyses on several hypervalent iodine compounds where the presence of I=O, I=N, and I=C bonds was questionable. The AdNDP approach for the analyses of the MO wave functions of the corresponding
compounds revealed only single I→X dative-bond character. The significant advancement made in the current study is that the bonding patterns and formulas are derived from the MO wave function by a unified and well-defined quantum chemical procedure. In particular, we believe that our representation of the studied hypervalent compounds might clarify the question of I–X double/single bond notation used in student courses and in current textbooks. We also believe that our theoretical findings can serve as a general guideline for the synthesis of new molecules with unusual bonds and reactivities.

9-1. Experimental section

The detailed description of the AdNDP algorithm developed by Zubarev and Boldyrev can be found elsewhere.\[9] From the computational point of view, AdNDP is a generalization of the NBO analysis by Weinhold.\[24] AdNDP performs analysis of the first-order reduced density matrix with the purpose of obtaining its local block eigenfunctions with optimal convergence properties for describing the electron density. The local blocks of the first-order reduced density matrix correspond to the sets of \(n\) atoms (from one to all the atoms of the molecule) which are tested for the presence of a two-electron object (\(nc-2e\) bonds, including core electrons and lone pairs as a special case of \(n=1\)) associated with this particular set of \(n\) atoms. The \(n\) atomic sets are formed and checked in an exhaustive manner, so that the recovered \(nc-2e\) bonding elements always correspond to the point group symmetry of the system after these bonding elements are superimposed onto the molecular frame. For the given \(n\) atomic block those eigenvectors are accepted whose occupation numbers (eigenvalues) exceed the
established threshold value, usually close to 2.00 $|e|$. Thus, Lewis’s idea of an electronic pair as the essential element of bonding is preserved. The AdNDP procedure is numerically efficient because it involves only a series of diagonalizations of density matrix blocks. It is unbiased in the sense that no preliminary ideas of the bonding pattern are required to perform analysis. The AdNDP code is a stand-alone program that uses output from Gaussian 09. The density matrix used for the basis of the natural atomic orbitals as well as for the transformation between atomic orbital and natural atomic orbital basis sets, which are used by the AdNDP program, was generated at the B3LYP/LANL2DZ$^{[25,26]}$ level of theory by means of the NBO code$^{[27]}$ incorporated into Gaussian 09.$^{[28]}$ It is known that the results of NBO analysis do not generally depend on the quality of the basis set, so the choice of the level of theory for the AdNDP application is adequate. The visualization of the results of the calculations was performed by using MOLEKEL 5.4.0.8.$^{[29]}$

References


[29] U. Varetto, Molekel 5.4.0.8, Swiss National Supercomputing Centre: Manno, Switzerland, 2009.
Figures

**Figure 9-1.** Common representation of hypervalent iodine compounds with I=X double bonds (structures 1–5) adopted in research literature and the polymeric structure of iodosylbenzene 6.

**Figure 9-2.** I) General representation of the IO$_4^-$ structure; II) Symbolic representation of IO$_4^-$ according to AdNDP; III) AdNDP bonding pattern of IO$_4^-$. The corresponding point group symmetry and spectroscopic state of IO$_4^-$ are given in parenthesis. ON stands for the occupation number here and elsewhere.
Figure 9-3. I) General representation of the PhIO structure; II) Symbolic representation of PhIO according to AdNDP. III) AdNDP bonding pattern for PhIO). The corresponding point group symmetry and spectroscopic state of PhIO are given in parenthesis.
Figure 9-4. I) General representation of the PhINSO$_2$Ar structure; II) Symbolic representation of PhINSO$_2$Ar according to AdNDP; III) AdNDP bonding pattern of the PhINSO$_2$Ph molecule on the I–N, S–N, and I–C fragments.

Figure 9-5. I) General representation of the PhIC(CO$_2$Me)$_2$ structure; II) Symbolic representation of PhIC(CO$_2$Me)$_2$ according to AdNDP; III) AdNDP bonding pattern of the PhIC(CO$_2$Me)$_2$ molecule on the I–C, C–C fragments.
Figure 9-6. Complete AdNDP analysis of chemical bonding in PhIO molecule.

Figure 9-7. Complete AdNDP analysis of chemical bonding in PhIO₂ molecule.
Figure 9-8. Complete AdNDP analysis of chemical bonding in PhIO$_3$ molecule.

PhIO$_3$ ($C_1, 'A'$)

- Three 2c-2e dative I-O σ bonds and 2c-2e I-C σ bond
  - ON = 1.91-2.00 |e|
- Three 1c-2e lone pairs on each O
  - ON = 1.80-1.99 |e|
- Five 2c-2e C-H and six C-C σ bonds
  - ON = 1.91-1.99 |e|
- Three 6c-2e π bonds
  - ON = 2.00 |e|
CHAPTER 10

ALL-METAL ANTIAROMATICITY IN Sb₄-TYPE LANTHANOCENE ANIONS¹

Abstract

Antiaromaticity, as introduced in 1965, usually refers to monocyclic systems with 4\(n\) \(\pi\) electrons. This concept was extended to all-metal molecules after the observation of \(\text{Li}_3\text{Al}_4^-\) in the gas phase. However, the solid-phase counterparts have not been documented to date. Herein, we describe a series of all-metal antiaromatic anions, \([\text{Ln}(\eta^4-\text{Sb}_4)_3]^3^-\) (Ln=La, Y, Ho, Er, Lu), which were isolated as the K([2.2.2]crypt) salts and identified by single-crystal X-ray diffraction. Based on the results obtained from the chemical bonding analysis, multicenter indices, and the electron-counting rule, we conclude that the core \([\text{Ln}(\eta^4-\text{Sb}_4)_3]^3^-\) fragment of the crystal has three locally \(\pi\)-antiaromatic Sb₄ fragments. This complex represents the first locally \(\pi\)-antiaromatic all-metal system in the solid state, which is stabilized by interactions of the three \(\pi\)-antiaromatic units with the central metal atom.

Aromaticity, a core concept of organic chemistry, was put forward by Kekulé 150 years ago to explain the unusual properties of benzene.¹ In 1931, Hückel formulated his famous \(4n + 2\) rule based on quantum-mechanical considerations of benzene.² It states that if a conjugated monocyclic hydrocarbon molecule has the right number of \(\pi\) electrons obeying this rule, then the molecule is aromatic and has high stability and low reactivity. More than thirty years later, Breslow introduced the concept of antiaromaticity

in his seminal paper,[3] which is the antonym of aromaticity and refers to systems with 4n electrons, low stability, and high reactivity. He wrote: “However, both theory and experiment suggest that for at least some members of the 4n series cyclic delocalization of \( \pi \) electrons leads to strong destabilization of the compound, in contrast to the stabilization characteristic of aromaticity. For these reasons we proposed the term "antiaromatic" to describe such systems.”[3b] Initially, the concepts of aromaticity and antiaromaticity were primarily confined to the realm of organic chemistry. However, with an improved quantum-mechanical understanding of the underlying phenomena, the aromaticity and antiaromaticity concepts have been extended beyond organic molecules. For example, based on the isoelectronic principle, borazine (\( \text{B}_3\text{N}_3\text{H}_6 \)) and 1,3,2,4-diazadiboretidine (\( \text{B}_2\text{N}_2\text{H}_4 \)) were considered to be inorganic analogues of the prototypical aromatic and antiaromatic molecules benzene and cyclobutadiene, respectively. Indeed, borazine exhibits many structural similarities to benzene, such as planarity and equivalent B−N bond distances.[4] However, on the basis of magnetic or other aromatic criteria, borazine was considered to be either weakly aromatic or nonaromatic.[5] Whereas the \( \text{B}_2\text{N}_2\text{H}_4 \) molecule has not been synthesized yet, five X-ray structures of substituted diazadiboretidines have been reported.[6] Whereas the cyclic \( \text{B}_2\text{N}_2 \) fragment was found to be planar (except for in the tetra-tert-butyl derivative), the synthesized \( \text{B}_2\text{N}_2\text{H}_4 \) derivatives do not follow the expected reactivity of antiaromatic molecules because they survive the thermal elimination of isobutene from the tert-butyl derivative.[6] The main reason why these inorganic “aromatic” and “antiaromatic” analogues do not follow the expected behavior is the difference in the electronegativities
of nitrogen and boron, resulting in the localization of the $\pi$ electrons on the more electronegative nitrogen atoms.\[^7\]

To discover inorganic aromatic or antiaromatic clusters, which could potentially be used as coordination ligands in solid-state compounds, molecules composed of the same type of atoms need to be considered as they would be more conducive to electron delocalization. Indeed, many such inorganic aromatic clusters, such as $E_5^{4-}$, $E_5^{6-}$ ($E=Si$, Sn, Pb), $Pn_5^-$, $Pn_4^{2-}$ ($Pn=P$, As, Sb, Bi), and $X_4^{2+}$ ($X=S$, Se, Te), have been reported.\[^7,8\]

One of the first examples of aromatic metal clusters obtained in the solid state was the triangular $Ga_3^{2-}$ ring embedded in a large organometallic molecule, as reported by Robinson and co-workers in 1995.\[^9\] In 2001, we reported the first example of an all-metal aromatic cluster, $Al_4^{2-}$, in the form of gaseous bimetallic clusters, namely $LiAl_4^-$, $NaAl_4^-$, and $CuAl_4^-$.\[^10\] Two years later, we synthesized and characterized the first all-metal antiaromatic cluster, $Al_4^{4+}$, in the form of $Li_3Al_4^-$ with four $\pi$ electrons.\[^11a\] The antiaromaticity of $Li_3Al_4^-$ was further discussed in terms of magnetic criteria.\[^11b\] Since then, a large number of aromatic and antiaromatic all-metal clusters have been observed in the gas phase.\[^12\] It is important to note that the synthesis of solid-state compounds with antiaromatic building blocks is understandably much more challenging because of their low stability and high reactivity. Thus far, we are not aware of any solid-state compounds containing all-metal $\pi$-antiaromatic building blocks. Recently, we reported an all-metal aromatic sandwich $Au$-$Sb$ cluster.\[^13\] In this context, delocalized $\pi$ bonding in each aromatic $Sb_3$ unit was induced by intramolecular electron transfers. Therefore, we were interested in whether a redistribution of valence electrons could happen in a conventional Zintl cluster $Sb_4^{2-}$ through stabilization by certain metal cations.
Moreover, Dehnen and co-workers have synthesized a handful of ternary intermetalloid cage-like anions, in which lanthanide atoms are encapsulated by mixed Group 13/15 or 14/15 cages.\cite{15} Their investigations show a delocalization of lone pairs in main-group metal frameworks toward the empty $d_{z^2}$ orbital of $\text{Ln}^{3+}$, which preliminarily confirmed the feasibility of introducing lanthanide ions into main-group clusters. In this work, we treated a new, but more reactive lanthanide compound, $\text{Ln}(\text{benzyl})_3(\text{THF})_3$, with the Zintl precursor $\text{K}_5\text{Sb}_4$ in pyridine solution, which led to the isolation of a family of complexes with an entirely new structure, $[\text{K}([2.2.2]\text{crypt})]_3[\text{Ln}(\eta^4-\text{Sb}_4)_3] \cdot 4\text{py}$ ($\text{py}=\text{pyridine}$; $\text{Ln}=\text{La}$ (1), $\text{Y}$ (2), $\text{Ho}$ (3), $\text{Er}$ (4), or $\text{Lu}$ (5)), which are governed by antiaromaticity. Quantum-chemical calculations indeed indicated that there is a redistribution of the valence electrons from the cyclo-$\text{Sb}_4$ units to $\text{Ln}^{3+}$.

Compounds 1–5, $[\text{Ln}(\eta^4-\text{Sb}_4)_3]^{3-}$, feature three all-metal $\pi$-antiaromatic $\text{Sb}_4$ rhombic units as coordination ligands, which are all very air-sensitive and have quasi-$D_{3h}$ symmetry, as shown in Figure 10-1 for $\text{Ln}=\text{La}$ (1). The lanthanide ion in $[\text{Ln}(\eta^4-\text{Sb}_4)_3]^{3-}$ is surrounded by three cyclo-$\text{Sb}_4$ units; this structure type is similar to lanthanocene, $\text{LnCp}_3$ ($\text{Cp}=\text{cyclopentadiene}$), except that there are equatorial interactions between adjacent cyclo-$\text{Sb}_4$ units (average $\text{Sb}–\text{Sb}$ distance: 3.036 Å in 1). These $[\text{Ln}(\eta^4-\text{Sb}_4)_3]^{3-}$ species represent the first all-metal binary lanthanide/main group anions as such structures have never been reported before. Owing to the isostuctural features of all $[\text{Ln}(\eta^4-\text{Sb}_4)_3]^{3-}$ species, only the data for 1 ($\text{Ln}=\text{La}$) will be presented and discussed.

Among the three $\eta^4-\text{Sb}_4$ units or the twelve $\text{Sb}$ atoms around the $\text{La}$ atom (Figure 10-1), there are two types of $\text{La}–\text{Sb}$ interactions: six to $\text{Sb}$ atoms in equatorial positions (between $\text{La}$ and $\text{Sb}1$, $\text{Sb}3$, $\text{Sb}5$, $\text{Sb}7$, $\text{Sb}9$, and $\text{Sb}11$), ranging from 3.4338(5) to
3.4735(5) Å, and another six interactions with Sb atoms in non-equatorial positions (between La and Sb2, Sb4, Sb6, Sb8, Sb10, and Sb12), with relatively short La–Sb distances of 3.2386(5) to 3.2634(5) Å. To the best of our knowledge, compounds with Ln–Sb bonds have rarely been reported. Only two compounds with the formula RLn–Sb (R=organic group) have been described. Molecular all-metal rare-earth polyanantimonide clusters have never been synthesized, whereas the analogous transition-metal polyanantimonide clusters have been intensively investigated. As a result of the lanthanide contraction, the average Ln–Sb distances decrease significantly across the Ho, Er, and Lu analogues (Figure 10-2). Furthermore, the contraction effect is also reflected in the dihedral angles in the cyclo-Sb4 units from La to Lu (Figure 10-3). The average Sb–Sb bond lengths (2.819 Å) within the cyclo-Sb4 units are comparable among all five complexes, and they are slightly longer than those in previously isolated Sb42− (2.750 Å). Three-dimensional views of the compounds are shown in Figure 10-4.

The uniform bond lengths and the deviation from planarity imply unique electronic structures in the cyclo-Sb4 units. To improve our understanding of the structure and bonding in the new [Ln(η4-Sb4)3]3− species, we performed chemical bonding analyses using the adaptive natural density partitioning (AdNDP) method. In brief, the AdNDP analyses revealed twelve s-type lone pairs on the twelve Sb atoms (Figure 10-5A), twelve classical 2c-2e Sb–Sb σ bonds (4 on each cyclo-Sb4 unit; Figure 10-5B), which are responsible for the bonding within the three separated cyclo-Sb4 blocks (Sb1–Sb4, Sb5–Sb8, and Sb9–Sb12), three 3c-2e σ bonds, which are responsible for the bonding between the three separate cyclo-Sb4 units in the equatorial plane, as well as for the interaction of La with the equatorial Sb atoms (La/Sb1/Sb11, La/Sb3/Sb5, and La/Sb7/Sb9, Figure 10-
5C), and six 5c-2e π bonds on the three LaSb$_4$ fragments (two 5c-2e π bonds on each fragment are shown in Figure 10-5D).

The two 5c-2e π bonds on each Sb$_4$ fragment are quite similar to the two 4c-2e π bonds in the distorted rectangular structure of a neutral Sb$_4$ cluster,$^{[19]}$ rendering the compounds π-antiaromatic according to Breslow’s 4n rule. Therefore, on the basis of the AdNDP analyses and the electron-counting rule, the [Ln($\eta^4$-Sb$_4$)$_3$]$^{3-}$ cluster contains three π-antiaromatic Sb$_4$ fragments. The question is why such unstable antiaromatic units should be present in lanthanocene-type anions. Essentially, the strong interactions between the antiaromatic cyclo-Sb$_4$ units with the central Ln atom help stabilize the whole [Ln($\eta^4$-Sb$_4$)$_3$]$^{3-}$ complex.

A simple electron count reveals that the Ln atom possesses a positive charge of 3+ in the ionic limit in all the [Ln($\eta^4$-Sb$_4$)$_3$]$^{3-}$ complexes, which would lead to a negative charge of 2− on each cyclo-Sb$_4$ block, as also confirmed by an effective oxidation-state analysis.$^{[19]}$ An aromatic Sb$_4^{2-}$ species with 6π electrons and a square-planar structure has previously been isolated.$^{[20]}$ However, the bonding situation in the cyclo-Sb$_4$ units in the [Ln($\eta^4$-Sb$_4$)$_3$]$^{3-}$ cluster is different from that in an isolated Sb$_4^{2-}$ dianion owing to the interactions between the Sb$_4$ units and the central Ln atom. To be more precise, there is appreciable equatorial Sb–Sb bonding between the neighboring cyclo-Sb$_4$ units, as well as between the cyclo-Sb$_4$ units and the central Ln atom, via the 3c-2e σ bonds in [Ln($\eta^4$-Sb$_4$)$_3$]$^{3-}$ (Figure 10-5C). In fact, approximately two electrons on each cyclo-Sb$_4$ unit participate in the formation of the 3c-2e intracluster equatorial bonds, thus leaving only four electrons for the π framework on the cyclo-Sb$_4$ unit. The rhombic distortion of the Sb$_4$ units can be considered as a direct consequence of its antiaromaticity. We believe
that the local π antiaromaticity of the Sb\textsubscript{4} units is also consistent with the very high air sensitivity and reactivity of all of the [K([2.2.2]crypt)]\textsubscript{3}[Ln(\eta^{4}\text{-Sb}_{4})\textsubscript{3}]-4py compounds.

Additional information on the antiaromaticity of the \textit{cyclo}-Sb\textsubscript{4} units could potentially be obtained on the basis of nucleus independent chemical shift (NICS) indices\textsuperscript{[21]} However, such an analysis by Tsipis\textsuperscript{[22]} showed that the Sb\textsubscript{4}\textsuperscript{2-} dianion is antiaromatic although it has six delocalized π electrons and a square-planar structure, which would be consistent with a π-aromatic cluster. We thus did not use NICS in this case as it may lead to spurious results. Therefore, we calculated the electronic multicenter indices (I\textsubscript{ring} and MCIs),\textsuperscript{[23, 24]} which were previously shown to give excellent results for organic,\textsuperscript{[23–25]} all-metal,\textsuperscript{[26]} and inorganic\textsuperscript{[27]} compounds, providing aromaticity trends that are superior to those furnished by NICS\textsuperscript{[28]} The multicenter calculations showed that the Sb\textsubscript{4} blocks are more similar to cyclobutadiene than to cyclobutane (Table 10-1). In fact, coordination of the three Sb\textsubscript{4}\textsuperscript{2-} moieties with the La\textsuperscript{3+} ion drastically reduces the aromaticity of the Sb\textsubscript{4} units and gives multicenter values that are very close to those of cyclobutadiene, an organic antiaromatic counterpart.

In conclusion, a family of all-metal antiaromatic complexes, [Ln(\eta^{4}\text{-Sb}_{4})\textsubscript{3}]\textsuperscript{3-} (Ln=La, Y, Ho, Er, Lu), have been synthesized and structurally identified; the Ln\textsuperscript{3+} ions are facially coordinated by three antiaromatic \textit{cyclo}-Sb\textsubscript{4} units. Chemical bonding analyses by AdNDP of the [Ln(\eta^{4}\text{-Sb}_{4})\textsubscript{3}]\textsuperscript{3-} complexes showed that the Sb\textsubscript{4} building blocks feature four π electrons and are thus antiaromatic according to Breslow’s 4\textit{n} rule. The calculated multicenter indices reveal strong resemblance with cyclobutadiene,\textsuperscript{[29]} thus confirming the antiaromatic character of the Sb\textsubscript{4} fragments. The stability of the [Ln(\eta^{4}\text{-Sb}_{4})\textsubscript{3}]\textsuperscript{3-} complexes was found to be due to interactions within the Sb\textsubscript{4} units and additional
interactions between the cyclo-Sb$_4$ units and the central lanthanide atom. The [Ln(η$_4$-Sb$_4$)$_3$]$_3$ complexes represent the first all-metal antiaromatic compounds to be made in the condensed phase. They have opened a new direction in the synthesis of novel bimetallic lanthanide compounds and will stimulate further investigations of antiaromaticity in inorganic chemistry and material science.

References


Tables and Figures

*Table 10-1.* $I_{\text{ring}}$ and MCI values for the Sb$_4^{2-}$ unit within [La(η$^4$-Sb$_4$)$_3$]$^{3-}$, cyclobutadiene and cyclobutane.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$I_{\text{ring}}$</th>
<th>MCI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb$_4^{2-}$ within [La(η$^4$-Sb$_4$)$_3$]$^{3-}$</td>
<td>0.0020</td>
<td>0.0013</td>
</tr>
<tr>
<td>C$_4$H$_4$</td>
<td>0.0024</td>
<td>0.0085</td>
</tr>
<tr>
<td>C$_4$H$_8$</td>
<td>0.0007</td>
<td>0.0035</td>
</tr>
</tbody>
</table>
Figure 10-1. The structure of \([\text{La}(\eta^4-\text{Sb}_4)_3]_3^–\) (1). Thermal ellipsoids set at 50\% probability. A) Top view of the central projection. B) Side view. Selected bond ranges: Bonds between La and equatorial Sb atoms: 3.4338(5)–3.4735(5) Å; bonds between La and non-equatorial Sb atoms: 3.2386(5)–3.2634(5) Å; Sb–Sb bonds in cyclo-(Sb1–Sb4): 2.8180(6)–2.8339(6) Å; Sb–Sb bonds in cyclo-(Sb5–Sb8): 2.8088(5)–2.8262(6) Å; Sb–Sb bonds in cyclo-(Sb9–Sb12): 2.8171(5)–2.8262(6) Å; bonds between equatorial Sb atoms: 3.0179(6)–3.0517(5) Å.

Figure 10-2. The tendency of Ln-Sb bond distances with increasing atomic number in \([\text{K}([2.2.2]\text{crypt})]_3[\text{Ln}(\eta^4-\text{Sb}_4)_3]·4\text{py}\) (Ln = La, Ho, Er, Lu). (The subscript “e” and “ne” represent the equatorial position and the non-equatorial position, respectively).
**Figure 10-3.** The decreasing dihedral angles of cyclo-Sb₄ along with increasing atomic number in [K([2.2.2]crypt)]₃[Ln(η⁴-Sb₄)₃]·4py (Ln = La, Ho, Er, Lu).

**Figure 10-4.** [K([2.2.2]crypt)]₃[Ln(η⁴-Sb₄)₃]·4py (Ln=La, Y, Ho, Er, Lu) viewed down the b axis. Hydrogen atoms were omitted for clarity.
**Figure 10-5.** Chemical bonding analysis of $[\text{La}(\eta^4-\text{Sb}_4)_3]^{3-}$ by the AdNDP method at the Def2-SVPD level of theory. A) The twelve s-type lone pairs (1c-2e bonds) on twelve Sb atoms (1 per Sb atom), shown superimposed onto the molecular framework. B) The twelve 2c-2e Sb–Sb $\sigma$ bonds, shown superimposed onto the molecular framework. C) The three 3c-2e $\sigma$ bonds, shown superimposed onto the molecular framework. D) Two 5c-2e $\pi$ bonds in one cyclo-Sb$_4$ unit. The four other 5c-2e $\pi$ bonds were omitted for clarity. ON stands for occupation number and is equal to 2.0 $|e|$ in an ideal case.
CHAPTER 11

PECULIAR ALL-METAL $\sigma$-AROMATICITY OF THE $[\text{Au}_2\text{Sb}_{16}]^{4-}$ ANION IN THE SOLID STATE

Abstract

Gas-phase clusters are deemed to be $\sigma$-aromatic when they satisfy the $4n+2$ rule of aromaticity for delocalized $\sigma$ electrons and fulfill other requirements known for aromatic systems. While the range of $n$ values was shown to be quite broad when applied to short-lived clusters found in molecular beam experiments, stability of all-metal cluster-like fragments isolated in condensed phase was previously shown to be mainly ascribed to two electrons ($n=0$). In this work, the applicability of this concept is extended towards solid-state compounds by demonstrating a unique example of a storable compound, which was isolated as a stable $[\text{K([2.2.2]crypt})]^+$ salt, featuring a $[\text{Au}_2\text{Sb}_{16}]^{4-}$ cluster core possessing two all-metal aromatic AuSb$_4$ fragments with six delocalized $\sigma$ electrons each ($n=1$). This discovery pushes the boundaries of the original idea of Kekulé and firmly establishes the usefulness of the $\sigma$-aromaticity concept as a general idea for both small clusters and solid-state compounds.

Although the original concept of aromaticity in chemistry was put forward by August Kekulé$^{[1]}$ more than 150 years ago, it currently occupies a massive niche in modern chemistry.$^{[2]}$ The concepts of $\pi$ aromaticity/antiaromaticity were primarily used to explain chemical bonding in organic compounds. Today, these terms are well used for

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a variety of molecules, including inorganic compounds. Alongside, these concepts have also gained huge popularity as more and more chemical species are being discovered, where delocalized bonding is used to describe the structures. In 1995, Robinson and coworkers reported$^{[3]}$ the synthesis of Na$_2$[[(2,4,6-Me$_3$C$_6$H$_2$)$_2$C$_6$H$_3$]Ga]$_3$ with two $\pi$ electrons delocalized over the three gallium atoms that make the system $\pi$-aromatic according to the Hückel rule. Recently, the first solid-state all-metal $\pi$-antiaromatic compounds [Ln($\eta^4$-Sb$_4$)]$_3^-$ (Ln = La, Y, Ho, Er, Lu) were synthesized and characterized.$^{[4]}$ The [U@Bi$_{12}$]$^3^-$ anion with similar geometry was reported very recently by Dehnen and co-workers.$^{[5]}$ The aromaticity/antiaromaticity concept was also extended to bare metal clusters found in the gas phase.$^{[6]}$ For the first time, the $\sigma$-aromaticity concept was shown to be applicable to small alkali metal and alkaline earth metal clusters.$^{[7]}$ Modern developments on aromaticity in various aromatic/antiaromatic chemical species composed of main-group elements and transition metals have been extensively reviewed elsewhere.$^{[8-11]}$

For all all-metal aromatic fragments that have been synthesized in the solid state up to date, there were only two delocalized electrons responsible for the $\sigma$-aromaticity of the compounds, as exemplified by the cases of Pd$_3^+$, Au$_3^+$, and TiSn$_2$ clusters.$^{[12-14]}$ Thus far, we are not aware of any solid-state compounds containing two all-metal $\sigma$-aromatic fragments involving six delocalized electrons each. Hence, the 6-$\sigma$-electron aromatic fragments found in the [Au$_2$Sb$_{16}$]$^{1^+}$ cluster in this study expand the family of storable aromatic metal clusters thus solidifying usefulness of the $\sigma$-aromaticity concept in the solid state.
The title complex \([\text{Au}_2\text{Sb}_{16}]^{4-}\) (1), crystallizes in the form of \([\text{K([2.2.2]crypt})]_4\cdot\text{1·4en}\) (Figure 11-1), was isolated from an ethylenediamine (en) solution of \(\text{K}_3\text{Sb}_7\), \(\text{Au(PPh}_3\text{)Ph}\), and 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo-[8.8.8]hexacosane ([2.2.2]crypt). As shown in Figure 11-2, complex 1 has a rod-like shape and two Au atoms inlaid on the surface of the Sb\(_{16}\) polyanion framework possessing quasi-C\(_2\) point group symmetry.

Each Au atom in 1 is coordinated by four Sb atoms, and the quadrangles formed by the coordinating Sb atoms are slightly deviated from the plane. In the AuSb\(_4\) units, the Sb-Au-Sb bond angles (Au and two neighboring Sb atoms) are in the range of 82.35–105.698 Å for Au1 and 82.67–107.968 Å for Au2. The two AuSb\(_4\) faces are almost parallel to each other. Hence, the core of complex 1 can be described as a distorted tetragonal prism made up of two AuSb\(_4\) species, which are further stabilized by Sb\(_4\) fragments on the sides (Figure 11-2). The Au–Sb bond lengths (2.69±0.02 Å) span a very narrow range, thus underlining the importance of Au–Sb interactions within the two AuSb\(_4\) units, and the bonds are slightly longer than those in recently reported \([\text{Sb}_3\text{Au}_3\text{Sb}_3]^{3-}\) (2.60 Å in average),\(^{[15]}\) but shorter than those in some organometallic compounds such as \((1,8\text{-naphthalenediyl})_2(\text{Ph}_2\text{Sb})\text{Au}\) (2.76 Å in average).\(^{[16]}\)

Sb polyanions have a lower bond dissociation energy than their lighter congeners and therefore undergo more easily cluster rearrangements and form various Sb\(_n\) species, though large Sb\(_n\) \((n>11)\) clusters are still rare. As a matter of fact, the Sb\(_{16}\) species in 1 represents the largest unfragmented Sb\(_n\) polyanion known that was isolated from solution (Figure 11-3). The Sb–Sb short distances range from 2.72 to 2.85 Å, which suggests presence of both normal single bonds (2.78–2.86 Å) and somewhat shorter single bonds...
according to Pyykkö[17]. Essentially, 1 may be viewed as two Sb₇ units coupled by a Sb₂ dumbbell and pulled together because of the interaction with two Au atoms. From a structural point of view, the Sb₁₆ cluster can be obtained through structural transformation from the P₁₆²⁻-like geometry[18] via bond cleavage and rotation (Figure 11-4). Noteworthy, such transformation is feasible due to the interaction of each Au atom with four neighboring Sb atoms constituting a somewhat distorted square. Interestingly, the [Au₂Sb₁₆]⁴⁻ cluster (as a separate gas-phase molecule) was computationally found to be a true minimum on the potential energy surface (at the PBE0/Def2-TZVPD level of theory) with all bond lengths and angles being pretty close to the experimentally observed values.

To clarify the electronic structure of complex 1, chemical bonding analysis was performed using the adaptive natural density partitioning (AdNDP) method at the PBE0/Def2-SVPD level of theory, which helped partitioning the electron density in terms of localized (Lewis objects) and delocalized bonding elements.[19] In brief, AdNDP found ten d-type electron lone pairs (LPs) on two Au atoms (five on each) with occupation numbers (ONs) in the range of 1.83–1.99 |e|; 16 s-type electron LPs on 16 Sb atoms with ON=1.93–1.97 |e|; two p-type electron LPs on two peripheral Sb atoms (Sb1 and Sb16) with ON=1.71 |e|; 19 classical two-center two-electron (2c-2e) Sb–Sb σ bonds (ON=1.93–1.98 |e|) responsible for the direct bonding between Sb atoms constituting the framework of the cluster (Figure 11-5). Surprisingly, AdNDP did not find either Au–Sb or Sb–Sb classical 2c-2e σ bonds on the two AuSb₄ fragments. Instead, the remaining 12 electrons were found to participate only in a delocalized bonding: there are three 5c-2e σ bonds with ON=1.86–1.99 |e| found within each quasi-planar AuSb₄ fragment.
Noteworthy, contribution of the 6s orbital of Au in the formation of the completely bonding orbital is assessed to be 39%. Essentially, these bonds (Figure 11-6) look like classical $\sigma$-aromatic bonds found for gas-phase clusters (e.g., in the $B_7^-$ cluster$^{[20]}$: one completely bonding and two bonds possessing one nodal plane (mutually perpendicular) with $n=1$ according to the $4n+2$ rule. A simple orbital diagram schematically explaining the observed 5c-2e bonds is shown in Figure 11-7.

Importantly, this observation is in concordance with the Au–Sb bond equalization in the two AuSb$_4$ fragments that supports the aromaticity pattern. However, as seen from the geometry of complex 1, these two AuSb$_4$ fragments are quite peculiar since they do not have equal Sb–Sb bond lengths as expected for aromatic systems. In order to test the importance of aromaticity in 1, we performed calculations for two simple model systems, [AuSb$_4$H$_8$]$^-$ and [Sb$_4$H$_8$]$^{2-}$. The first cluster (Figure 11-8) has the same number of electrons in the AuSb$_4$ fragment as 1, but is free from the geometrical constraints, which are deemed to cause unequal Sb–Sb bond lengths. The second cluster is even simpler as it does not have a metal atom in the center but still is deemed to be aromatic based on the electron-counting rule and square-like geometry (Figure 11-9). Pronounced similarity in the geometries and electronic structures of the AuSb$_4$ fragment of the experimental complex 1 and the model clusters clearly confirms the $\sigma$-aromaticity pattern in these systems. Similarly to the case of Al$_4$$^{2-}$$^{[6]}$ atoms forming aromatic fragments in both compound 1 and the two model clusters are held together exclusively by delocalized bonds (Figures 11-10 and 11-11).

We did not use nucleus-independent chemical shift indices (NICS)$^{[21]}$ for our analysis as they may lead to spurious results for this particular cluster. Instead, in order to
probe aromaticity further we calculated the electronic multicenter indices ($I_{\text{ring}}$ and MCI$s$),$^{[22-24]}$ which were previously shown to give excellent results for all-metal$^{[25]}$ compounds and to provide aromaticity trends that are superior to those furnished by NICS.$^{[26]}$ The multicenter calculations also showed that there is some delocalization of electron density between the four Sb atoms of 1 and the [AuSb$_4$H$_8$]$^-$ system, which is compatible with a certain aromatic character of this unit. In particular, the delocalization occurs through a zigzag pattern, Sb6-Sb10-Sb9-Sb4 or Sb9-Sb6-Sb10-Sb4, like in Al$_4^{2-}$.$^{[6]}$ The MCI values of the Sb$_4$ units in these systems ($4.2 \times 10^{-3}$ and $8.3 \times 10^{-3}$, respectively) are not as large as in the [Sb$_4$H$_8$]$^{2-}$ model ($40 \times 10^{-3}$), but the values cannot be overlooked and indicate an incipient aromatic character.

In summary, the [Au$_2$Sb$_{16}$]$^{4-}$ (1) complex was isolated as stable [K([2.2.2]crypt)]$^+$ salt and identified by single-crystal X-ray diffraction. The rod-like Sb$_{16}$ framework in the anion represents the largest unfragmented Sb$_n$ polyanion isolated from solution, which is possible due to the $\sigma$-aromatic stabilization through quenching with two Au atoms, which participate in delocalized bonding to form two quasi-planar AuSb$_4$ $\sigma$-aromatic fragments. Data obtained from the analysis of the electronic structures of 1, and the model clusters [AuSb$_4$H$_8$]$^-$ and [Sb$_4$H$_8$]$^{3-}$ as well as the electronic indices of these systems proved that the two quasi-planar AuSb$_4$ moieties in 1 are indeed $\sigma$-aromatic due to the interaction of the Au atom with four neighboring Sb atoms in a delocalized manner. Thus, the [Au$_2$Sb$_{16}$]$^{4-}$ anion is the first solid-state all-metal $\sigma$-aromatic cluster that possesses two peculiar $\sigma$-aromatic AuSb$_4$ fragments featuring six delocalized $\sigma$ electrons each, which separately satisfy the Hückel rule of aromaticity. That pushes the boundaries of the
original idea of August Kekulé and proves the beauty and power of the σ-aromaticity concept in its generality: from short-lived gas-phase or matrix-isolated clusters to storable solid-state compounds. The discovery is especially important since the sextet of delocalized electrons was initially set at the heart of the aromaticity concept.

References


Figures

**Figure 11-1.** Crystal structure of [K([2.2.2]crypt)]$_4$[Au$_2$Sb$_{16}$]·4en down the $a$ axis.

**Figure 11-2.** Thermal ellipsoid plot of complex 1 (drawn at 50% probability). Selected bond lengths (Å) and angles (°): Au1–Sb5 2.6745(16), Au1–Sb8 2.6835(15), Au1–Sb11 2.6736(15), Au1–Sb12 2.6784(17), Au2–Sb4 2.7060(17), Au2–Sb6 2.6748(15), Au2–Sb9 2.6864(17), Au2–Sb10 2.6684(17), Sb8–Sb9 2.8193(17); Sb5–Au1–Sb12 162.77(5), Sb8–Au1–Sb11 162.58(5), Sb6–Au2–Sb10 162.24(6), Sb4–Au2–Sb9 159.38(5). Sticks between atoms serve the visualization and do not necessarily represent single bonds here and elsewhere.
Figure 11-3. Typical ligand-free Sb polyanions crystallized from solutions.
Figure 11-4. Schematic structural evolution from $P_{16}^{[13]}$ to $Sb_{16}$. a) Bond cleavage of 1–4. b) Rotation of $P_2$ in the middle for $90^\circ$ and $P_7$ on the left for $180^\circ$. c) $Sb_{16}$. 
Figure 11-5. Localized elements of chemical bonding elements deciphered for the [Au$_2$Sb$_{16}$]$^{4+}$ complex via AdNDP. a) 10 d-type electron lone pairs (LPs) on two Au atoms with ON= 1.83-1.99 |e|, b) 16 s-type LPs on 16 Sb atoms with ON=1.93-1.97 |e| (shown superimposed onto the molecular framework). c) 2 p-type LPs on two peripheral Sb atoms (Sb1 and Sb16) with ON=1.71 |e| (shown superimposed onto the molecular framework). d) 19 classical 2c–2e Sb–Sb σ bonds with ON=1.93-1.98 |e| constituting connected framework of Sb$_{16}$ polyanion (shown superimposed onto the molecular framework). e) Simplified representation of all single bonds constituting the Sb$_{16}$ framework.
Figure 11-6. Delocalized chemical bonding elements deciphered for complex 1. Six 5c-2e delocalized σ bonds with ON=1.86-1.99 |e| found at the a) upper AuSb$_4$ (Au1–Sb5–Sb8–Sb11–Sb12) and b) lower AuSb$_4$ (Au2–Sb4–Sb6–Sb9–Sb10) fragments.

Figure 11-7. The orbital diagram schematically explaining observed 5c-2e σ bonds over the square-like AuSb$_4$ fragments. (a) One fully bonding (no nodal planes) 5c-2e σ bond composed of the 6s orbital of Au and four 5p orbitals of Sb atoms. (b) Two degenerate 5c-2e σ bonds with one nodal plane (mutually perpendicular to each other) composed of 5p orbitals of Sb atoms.
Figure 11-8. Geometry of the [AuSb₄H₈]⁻ (D₂d, ¹A₁) model cluster at the PBE0/Def2-TZVPD level of theory. R(Au–Sb)=2.68 Å, R(Sb–Sb)=3.80 Å, R(Sb–H)=1.72 Å, ∠(Sb–Au–Sb)=90.3°, dihedral angle is 11.95°. Sticks between atoms help visualization and do not necessarily represent single bonds here and elsewhere.

Figure 11-9. Geometry of the [Sb₄H₈]²⁻ (D₂d, ¹A₁) model cluster at PBE0/Def2-TZVPD. Rₚₚₑₚₑₚₑₚₑₚₑₚₑ_(Sb–Sb)=3.24 Å, Rₜₜₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒₒ_o
Figure 11-10. Chemical bonding pattern revealed for the [AuSb$_4$H$_8$]$^-$ cluster via AdNDP. 

a) Five d-type lone pairs on Au atom with ON=1.78–2.00 $|e|$. b) Four s-type lone pairs on four Sb atoms with ON=1.99 $|e|$. c) Eight classical 2c–2e Sb–H $\sigma$ bonds with ON= 1.99 $|e|$. d) Three 5c-2e $\sigma$ bonds responsible for the bonding between one Au and 4 Sb atoms with ON=1.97–1.99 $|e|$. 
**Figure 11-11.** Chemical bonding pattern revealed for the [Sb₄H₈]²⁻ cluster via AdNDP. a) Four s-type lone pairs on four Sb atoms with ON=2.00 |e|. b) Eight classical 2c–2e Sb–H σ bonds with ON=1.99 |e|. c) Three 4c–2e Sb₂ σ bonds responsible for the bonding within 4 Sb atoms with ON=1.97-1.99 |e|. 
CHAPTER 12
SUMMARY

Significantly expanded computational capabilities have stimulated the rapid development of novel theoretical methods designed for chemical bonding analysis. Such methods provide qualitative and/or quantitative insights into the bonding patterns, which can further be used for the rational design of novel species with tailored properties. The research presented in this dissertation is focused on the investigation of chemical bonding in a very diverse set of chemical systems: from tiny sub-nano scale clusters (0D) observed in a molecular beam (PES experiments) to periodically extended chains of atoms (1D), one-atom-thin layers of various composition (2D), and novel compounds synthesized in a condensed phase (3D). For most of the systems, chemical bonding analyses were performed by means of the recently developed state-of-the-art AdNDP and SSAdNDP methods, designed for deciphering chemical bonding in molecular species (molecules, clusters, nanoparticles) and systems with periodic symmetry, respectively. Importantly, in some cases theoretical models developed on the basis of the AdNDP/SSAdNDP analyses were used as a guideline for further rational design of novel chemical species, thus demonstrating the predictive power of such calculations, and their fundamental importance for materials science in general. It is worthy to note that many of the works presented in this dissertation have been highlighted in various media outlets (including Chemical & Engineering News magazine), which demonstrate their exceptional impact on scientific community in the US and other countries. The detailed achievements of this dissertation are summarized below.
Using the concept of electronic transmutation,\(^1\) we have theoretically probed the existence of molecular chains formed by aluminum atoms in the example of two clusters: Li\(_2\)Al\(_2\)H\(_6\) and Li\(_3\)Al\(_3\)H\(_8\).\(^2\) It has been found that these inorganic chains are isostructural with ethane/disilane/digermane and propane/trisilane/trigermane molecules, respectively. NBO and AdNDP analyses have determined that one Al atom acquires approximately one electron from Li atom that enables the transmutation of Al into the Group 14 element. This finding is fundamentally important since it has been shown for the first time that electronic transmutation enables aluminum atoms to homocatenate with the formation of chain-like species resembling Group 14 hydrides. Thus, we have firmly established a new class of stable aluminum-chained compounds with the general formula Li\(_n\)Al\(_n\)H\(_{2n+2}\).

Importantly, this work has opened the door to the consequent experimental observation\(^3\) of the proposed compounds by means of the PES technique. The Bowen group has produced more than two hundred novel aluminum hydrides promising to have applications as highly energetic materials.\(^4\)\(^-\)\(^7\) Using their expertise, they have managed to produce a negatively charged Li\(_2\)Al\(_3\)H\(_8\)\(^-\) cluster, which is isoelectronic to the proposed Li\(_3\)Al\(_3\)H\(_8\). Our joint experimental and theoretical study has elucidated the most stable isomer contributing to the PES spectrum, and confirmed presence of the Al–Al–Al chain, thus verifying the proposed structure and its chemical bonding pattern.\(^3\) We are hopeful that if synthesized in bulk, this newly designed compound could be utilized as a hydrogen storage material, reducing agent, or energetic material.

In another joint experimental and theoretical study we found a very unique cluster that pushed the limits of structural chemistry. The Wang group has produced an anionic cluster composed of 16 boron atoms and one cobalt atom in a molecular beam, and
recorded its PES spectra. Global minimum searches have reliably established two most stable atomic configurations for the CoB$_{16}^-$ cluster that turned out to be almost energetically degenerate on the potential energy surface at various levels of theory. Their structures are unprecedented in chemistry and reminiscent of drums made out of two B$_8$ rings sandwiching a Co atom. Due to such unusual coordination, the most symmetrical isomer achieves a record-high coordination number of 16 for an atom. Importantly, for the first time we have shown that doping of boron cluster with a transition metal atom “catalyzes” an earlier 2D-to-3D structural transition in anionic boron clusters, which researches have sought for a long time. AdNDP analysis of chemical bonding helped explain the stability of these remarkable tubular clusters. According to it, double σ- and π-aromaticity as well as delocalized bonding interactions of the 3d AOs of Co with the B$_8$ rings are essential for the formation of such structures. We believe that observation of the CoB$_{16}^-$ cluster opens further possibilities for designing novel boron-based nanomaterials since the CoB$_{16}^-$ drums can be considered as the embryos for boron nanotubes.

Based on the chemical bonding pattern, a novel stable triple-decked [CoB$_{16}$(CaCp)$_2$]$^-$ sandwich was proposed as a promising route for the realization of CoB$_{16}^-$ in the solid state. It is worthy to point out that the AdNDP analysis of chemical bonding has not only helped us understand its electronic structure, but also provided us with a possibility to propose another molecular drum, which could be experimentally observable. Using this knowledge, a very similar MnB$_{16}^-$ cluster (slightly distorted due to the Jahn-Teller effect) was proposed and experimentally observed. Further, chemical bonding models developed for these clusters have helped rationally design larger doped-boron clusters with even higher coordination. Recently, the Wang group has reported
experimental observation of RhB$_{18}^-$ and TaB$_{20}^-$ drum-shaped clusters,\textsuperscript{13,14} which set the record of coordination numbers in chemistry to 18 and 20, respectively.

In addition to the investigation of gas-phase clusters, this dissertation also reports joint experimental and computational studies of clusters and molecules made in a condensed phase.

While in the majority of textbooks and papers on hypervalent iodine compounds\textsuperscript{15–19} bonds between iodine and oxygen, iodine and nitrogen, and iodine and carbon follow a double bond notation, AdNDP analysis of chemical bonding in such molecules showed very interesting and controversial results. In contrast to the common and chemically intuitive I=X (X=O, N, C) double-bond representation, AdNDP suggested that these bonds are single, with the iodine atom donating one electron pair to O, N, or C.\textsuperscript{20} We are inclined to believe that this finding appears to be a more general trend in chemistry, and is akin to the bonding pattern in well-known oxyanions, such as sulfate, nitrate, and phosphate anions where an oxygen atom accepts one electron pair from S, N, or P to form a corresponding single bond.

Cryptands (synthetic bi- and polycyclic multidentate ligands),\textsuperscript{21} being more expensive and difficult to prepare, offer much better selectivity and strength of binding\textsuperscript{22} than other complexants for alkali metals, such as crown ethers. Our collaborators (the Sun group) have synthesized two very unusual clusters\textsuperscript{23,24} that were isolated as stable [K([2.2.2]crypt)]$^+$ salts. The aesthetically pleasing and unexpected geometric structures of the Sb$_4$-type lanthanocene anion clusters\textsuperscript{23} ([Ln($\eta^4$-Sb$_4$)$_3$]$^{3-}$ (Ln=La, Y, Ho, Er, Lu)) were explained via the chemical bonding analysis, which showed a very peculiar bonding pattern. According to it, three Sb$_4$ units in [Ln($\eta^4$-Sb$_4$)$_3$]$^{3-}$ are all locally $\pi$ antiaromatic.
Essentially, these compounds represent the first examples of all-metal locally π antiaromatic units realized in the solid state. The second anion cluster\textsuperscript{24} ([Au\textsubscript{2}Sb\textsubscript{16}]\textsuperscript{4−}) was also shown to be very unusual. According to AdNDP, the formation of the largest unfragmented Sb\textsubscript{16} framework isolated from solution is possible due to the σ-aromatic stabilization through quenching with two Au atoms, which participate in delocalized bonding to form two quasi-planar AuSb\textsubscript{4} σ-aromatic fragments. Thus, the [Au\textsubscript{2}Sb\textsubscript{16}]\textsuperscript{4−} anion represents the first all-metal σ aromatic cluster in a solid state with two 6-σ-electron aromatic fragments that pushes the boundaries of the original idea of August Kekulé\textsuperscript{25} and proves the beauty and power of the σ aromaticity concept in its generality: from short-lived gas-phase or matrix-isolated clusters to bottleable solid state compounds.

The rest of the projects presented in this dissertation are devoted to the deciphering chemical bonding in systems with periodic symmetry. Two of such systems are well known and experimentally observed (graphene\textsuperscript{26}, BC\textsubscript{3} sheet\textsuperscript{27}) while the other two are theoretically predicted materials awaiting their experimental realization ((SF\textsubscript{4}−SF\textsubscript{4})\textsubscript{∞} chain\textsuperscript{28}, Cu\textsubscript{2}Si sheet\textsuperscript{29}).

For a chemical bonding analysis in graphene\textsuperscript{30} we have used a fragmental approach by constructing various model fragments of the infinitely extended graphene and adding the external charges on them in order to preserve the number of π-electrons of the ideal graphene lattice. For every model cluster we have found that in addition to the classical C–C σ bonds constituting the honeycomb structure, there are two π-electrons located over every hexagon ring. The Hückel 4n+2 π-electrons rule\textsuperscript{31} supports the idea of aromaticity in each hexagon ring in these fragments. Overall, it was concluded that
graphene is locally aromatic, and its aromaticity is different from the aromaticity in benzene,$^{32}$ coronene,$^{33}$ or circumcoronene.$^{33}$

Based on this chemical bonding model, we were able to explain the structure and chemical bonding of a different monolayer, which might be considered as a derivative of graphene. The substitution of every fourth carbon atom in graphene by boron preserves the completely planar honeycomb geometry and leads to the formation of the BC$_3$ lattice, which was experimentally confirmed to adopt rather symmetrical atomic configuration, where six boron atoms surround each carbon hexagon. In addition to the classical C–C σ bonds constituting the carbon hubs, and B–C σ bonds responsible for the direct bonding between these hexagons, AdNDP revealed that two π-electrons found over every hexagon in graphene migrate in BC$_3$ to hexagons composed of carbon atoms only. This results in six π-electrons over each C$_6$ fragment.$^{34}$ Since such pattern is reminiscent of the one found for the stable benzene molecule, we have called this process “benzation”, thus explaining the formation of the benzene-like stability islands, responsible for the overall system stabilization. Importantly, this finding has promoted the prediction of the completely different 2D systems (C$_2$X (X=H, F, Cl)).$^{35}$ These functionalized graphene monolayers feature benzene-like fragments too, and were found to be more stable than any other previously proposed structures of the corresponding stoichiometry and composition.

Inspired by the structure of the S$_2$F$_{10}$ molecule exhibiting direct S–S bond and its high kinetic stability, we tested the viability of extended M$_n$F$_{4n+2}$ molecules (M=S, Se; n=2–9) featuring chain-like M–M bonding as well as infinitely long systems using periodic boundary conditions.$^{28}$ The studied high-symmetry molecules were found to be
minima on the potential energy surface for $S_nF_{4n+2}$ ($n=2-9$) and up to $n=6$ for selenium analogs, while showing good kinetic stability too. Experimentally confirmed high stability of $S_2F_{10}$ provides us with a hope that the studied molecules can be synthesized too. Phonon calculations of the corresponding periodic structures confirmed a dynamic stability of the $-(SF_4-SF_4)_{\infty}$ chain, whereas analogous $-(SeF_4-SeF_4)_{\infty}$ chain is found to have a number of imaginary phonon frequencies. SSAdNDP analysis of the $-(SF_4-SF_4)_{\infty}$ chain has revealed direct S–S $\sigma$ bonds and S–F $\sigma$ bonds. We have proposed a novel definition and, subsequently, novel abbreviation (ENAC) by the analogy with extended metal atom chain (EMAC) complexes. We hope that our work will inspire experimentalists to synthesize these interesting one-dimensional chemical species and find new compounds belonging to the ENAC family.

Using periodic boundary conditions and reduced dimensionality we showed that Cu and Si atoms can be stabilized in a very unusual manner by forming a novel 2D Cu$_2$Si material, which features unprecedented hypercoordinate arrangement. Chemical bonding analysis has shown absence of any direct classical Cu–Si bonds. Instead, SSAdNDP revealed that only delocalized $4c$-$2e$ $\sigma$ bonds are responsible for the planar geometry of the Cu$_2$Si sheet. It is worthy to note that this discovery has spurred researchers to explore novel nano-materials on the basis of this hexacoordinate material. Thus, very recently a series of Cu$_2$Si nanotubes with various diameters, chiral vectors and morphologies were proposed. Researches are optimistic that these nanotubes are promising candidates to envision application as metallic connections in nanoscale electronic devices.
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Appendix A – Permission letters for journal copyright release

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February 8, 2017

Dear Ivan A. Popov,

This letter is to confirm that you have my permission to use the following papers in part or in full for preparation or presentation of your dissertation:


Sincerely,

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J. Tyler Gish  
February 8, 2017

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Dear Ivan A. Popov,

This letter is to confirm that you have my permission to use the following papers in part or in full for preparation or presentation of your dissertation:


Sincerely,

Lei-Jiao Li
CURRICULUM VITAE
Ivan A. Popov
(March 15, 2017)

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RESEARCH AND EDUCATIONAL BACKGROUND

Ph.D. Chemistry 2011-2017
Department of Chemistry and Biochemistry, Utah State University
Graduate Advisor: Dr. Alexander I. Boldyrev
Visiting Graduate Research Assistant. Computational Materials Science 11/2016
University of California, Los Angeles
Advisor: Dr. Anastassia Alexandrova

Peoples’ Friendship University of Russia (PFUR), Moscow
Graduate Advisor: Dr. Konstantin V. Bozhenko

Peoples’ Friendship University of Russia (PFUR), Moscow
Undergraduate Advisor: Dr. Konstantin V. Bozhenko
AWARDS AND HONORS

College of Science Ph.D. Graduate Researcher of the Year, USU 2017

Marjorie H. Gardner Teaching Award, USU 2016

Oral Presentation Winner at the Student Research Symposium, USU 2016

Outstanding Graduate Student in Chemistry Award, USU 2015

Award for Early Research Progress in Chemistry, USU 2013

M. Sc. Honor Diploma (*Summa cum laude*), PFUR 2011

Best Bachelor's Degree Diploma, PFUR 2009

Dr. Gryaznov Memorial Award for Excellence in Science, PFUR 2009

B. Sc. Honor Diploma (*Summa cum laude*), PFUR 2009

Scholarship for Outstanding Academic Achievements, PFUR 2004-2011

Winner of the Local Olympiad in Chemistry, Sibay, Russia 2004

GRANTS

Graduate Research and Collaborative Opportunities Grant 2016

*Role: PI. Investigators: Ivan A. Popov (PI)*

U. S. National Science Foundation (CHE-1664379), Pending 2016

Role: Ph.D. Investigator. Investigators: Alexander I. Boldyrev (PI) Ivan A. Popov (Ph.D.)

TEACHING EXPERIENCE

CHEM 1220. Principles of Chemistry II (Recitations for Majors), USU    Spring 2015

CHEM 1215. Principles of Chemistry I (Lab Instructor), USU    Springs 2013-2016

CHEM 1210. Principles of Chemistry I (Recitation Instructor), USU    Spring 2012

Utah State University Teaching Assistant Workshop, USU    Summer 2011

College Level Chemistry Teaching, PFUR    Fall 2010

PROFESSIONAL ACTIVITIES

Organizer:

International Conference on Chemical Bonding 2016, Lihue, HI    07/2016

International Conference on Chemical Bonding 2017, Lihue, HI    06/2017

Peer Reviewer:

Journal of the American Chemical Society; Nature Communications; Chemical Science; Nanoscale; Physical Chemistry Chemical Physics; The Journal of Physical Chemistry; Chemical Physics Letters (Recognized Reviewer Status); Chemistry – An Asian Journal.
Expert:


Membership: American Chemical Society (ACS) 2011-present

CONFERENCE PRESENTATIONS AND SEMINARS

Materials Science & Technology 2016. “Chemical Bonding in Graphene and Newly Predicted Two-Dimensional Materials”. Salt Lake City, UT (Talk)

4th International Conference on Chemical Bonding (ICCB-2016). “Unique Cases of Chemical Bonding in Clusters and Solids: Localized and Delocalized Bonding Patterns”. Lihue, HI (Invited Talk, Presiding Chair)

Student Research Symposium 2016. “Cobalt-Centred Boron Molecular Drums: the Highest Coordination Number in Chemistry”. Logan, USU (Oral Presentation)


249th National ACS Meeting & Exposition. “Combined Photoelectron Spectroscopy and ab initio Studies of Pure, Carbon-Doped, and Transition-Metal-Doped Boron Clusters”. Denver, CO (Poster)
“Complexes Between Planar Boron Clusters and Transition Metals: a Photoelectron Spectroscopy and \textit{ab initio} Study of CoB\textsubscript{12}\textsuperscript{−} and RhB\textsubscript{12}\textsuperscript{−}”. Salt Lake City, UT (\textbf{Poster})

\textbf{Chemistry and Biochemistry Departmental Seminar.} “Joint PES and \textit{ab initio} Studies of Pure and Doped Boron Clusters”. Logan, UT (\textbf{Talk})

\textbf{Physical and Analytical Chemistry Seminar.} “Structure and Chemical Bonding of Anionic Boron Clusters: From B\textsubscript{3}\textsuperscript{−} to B\textsubscript{25}\textsuperscript{−}”. Logan, UT (\textbf{Talk})

\textbf{245\textsuperscript{th} National ACS Meeting \& Exposition.} “Chemical Bonding in Graphene, its Derivatives, and Several Polycyclic Aromatic Hydrocarbons”. New Orleans, LA (\textbf{Poster})

\textbf{PUBLICATIONS}

(March 15, 2017)

Sum of the times cited: \textbf{502} (Google Scholar) since 2012. \textit{H-index=13}.


*Impact Factor = 22.00, Times Cited: 102*. **Invited Review**


*Times Cited: 2*. **Invited Chapter**


*Impact Factor = 2.89, Times Cited: 26*. **Article**


*Impact Factor = 1.85, Times Cited: 3*. **Article**


[18] **I. A. Popov**, X. Zhang, B. W. Eichhorn, A. I. Boldyrev, K. H. Bowen, Aluminum Chain in Li$_2$Al$_3$H$_8$ as Suggested by Photoelectron Spectroscopy and *ab initio*


