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Recent Advances in Aromatic Antimony Clusters

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ABSTRACT This paper highlights the compounds containing Sb cluster fragments, either synthesized in the solid-state, discovered from the gas phase, or only theoretically predicted. These Sb_n clusters feature unique chemical bonding, fascinating structures, and special stabilities that can be well rationalized by aromaticity or antiaromaticity. A deep understanding to their electronic structures is essential and will greatly facilitate the experimental synthesis of new Sb_n cluster-based materials.

KEYWORDS Aromaticity, Antiaromaticity, Sb clusters, Chemical Bonding

Contents

1. Introduction

More than 150 years ago, August Kekulé proposed the concept of aromaticity to rationalize the unusual low reactivity and high stability of benzene.[1,2] In 1931, Erich Hückel introduced the 4n+2 rule to further explain the aromaticity of cyclic molecules, especially benzene, which has six delocalized π-electrons.[3] In 1965, Ronald Breslow proposed the concept of antiaromaticity to define planar carbon rings with 4n π-electrons that have low stability and high reactivity.[4,5] Since then, aromaticity and antiaromaticity have become new territories in chemistry.

Initially, the concept of aromaticity was solely limited to organic chemistry for characterizing planar conjugated compounds. But in the late 20th century, the concept of aromaticity was extended to inorganic compounds.[6-13] In 1995, Robinson and coworkers isolated the sodium salt of a phenyl-substituted Ga_3 ring with two π-electrons, which is an isoelectronic species of the hydrocarbon analogue $C_3H_3^+$, and thus serves as the first good evidence for metal aromaticity.[14] Subsequently, Twamley and Power successfully isolated $K_2[Ga_4(C_6H_3\text{-}2,6\text{-}Trips_2)_2]$ (Trip=C_6H_2-2,4,6-$^iPr_3$), and its square-planar Ga_4 unit with two π electrons is similar to $C_4H_4^{2+}$.[15-17] Afterwards, a large number of metal clusters featuring aromaticity have been theoretically predicted, such as Sb_4^{2-}, Bi_4^{2-}, As_5^-, Sn_5^{6-} and Pb_5^{6-}, which are valence isoelectronic to their prototypes, namely aromatic hydrocarbon $C_4H_4^{2-}$ and $C_5H_5^-$.[18-23] In 2001, Wang, Boldyrev and coworkers discovered the first all-metal aromatic cluster, Al_4^{2-}, by laser vaporization and characterized its square Al_4 ring structure and two π-electron aromaticity nature by comparing the experimentally measured and the computed vertical electron detachment energies.[24] In the same year, they addressed a square-planer fragment Hg_4^{6-} in the solid Na_3Hg_2 amalgam compound and concluded that its structural stability actually is due to the all-metal aromaticity based on careful theoretical analysis.[13] Two years later, the same group reported the first example of an all-metal π-antiaromatic gaseous cluster, Al_4^{4-}, in the form of Li_3Al^{4-}. This cluster has four π electrons and rectangular Al_4 ring,[25] but its σ-aromaticity helps stabilize the cluster.[26]

In 2001, Hirsch and co-workers proposed the spherical aromaticity of inorganic cage molecules, and used the $2(N + 1)^2$ counting rule to rationalize their molecular structures and properties.[12] Their theoretical analyses showed that variety of Zintl anions, such as Ge_4^{4-}, Si_4^{4-}, Pb_4^{4-} and Sn_4^{4-},[27-29] which are isoelectric with Td symmetrical Bi_4, Sb_4, As_4 and P_4, are doubly aromatic [30, 31] since both σ and π-subsystems satisfy the $2(N + 1)^2$ rule. In general, the complete filling of σ and π shells results in the symmetrically distributed angular momentums, and very likely a stable cluster with spherical aromaticity.[32] In contrast, incomplete filling of those shells is accompanied by asymmetric distribution of the angular momentum, leading to reduction of aromaticity, as in the case of cage-like P_4^{2-} (with a lower symmetry of C_{2v}) or even establishment of antiaromaticity. They also described that D_{3h} symmetrical *closo*-cages Si_9^{4-},[33-34] Ge_9^{3-},[35-41] Sn_9^{4-},[12,37,42-45] Pb_9^{4-}[Error! Bookmark not defined.,38, 46-50] and Bi_9^{5+} [50] represent energy minima and do not obey wade's rule. The stability of these cages could be attributed to $2(N + 1)^2$ double spherical aromatic configuration of their valence electrons containing 8 π (N_π = 1) and 32 σ electrons (N_σ = 3).

In last two decades, various efforts have been given on group-15 clusters, especially E_4^{2-} (E = P, As, and Sb), to understand how the chemical bonding is related to electronic structures and stability from the view of electron delocalization. Joint theoretical and experimental studies revealed that the lowest-energy isomer of E_4^{2-} adopts a D_{4h} symmetrical planar structure holding six π-electrons, and the aromaticity helps thermodynamically stabilize these molecules.[51] Especially, the successful synthesis of the carbon-free sandwich structure, $[Ti(\eta^5\text{-}P_5)^2]^{2-}$,[9] ignited the great research interests into the sandwich complexes with inorganic group-15 ring ligands, in particular, for the aromaticity enhanced stability.

In this paper we will summarize the most recent studies on aromaticity, antiaromaticity and σ aromaticity of all-metal clusters involving Sb_n fragments discovered in condensed phase or gas phase. Some theoretically predicted but not-yet- synthesized clusters will also be discussed.[52] Special attention will be given to highlight the importance of using aromaticity/ antiaromaticity concepts to develop related compounds with unique chemical bonding and properties.

2. All-metal sandwich-type compounds with π-aromaticity

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In the beginning of 1950s, the first sandwich compound $(C_5H_5)_2Fe$, termed "ferrocene" (Fig. 1A) was synthesized.[53-57] This breakthrough discovery introduced a new concept of π-bonding of carbocyclic rings to metal atoms, opened new research disciplines in materials science and chemistry, and led to fabulous applications in material precursors, catalysis and chemical synthesis.[58]

Theoretical studies greatly facilitated the development of the inorganic sandwich compounds. In 2001, Frenking and coworkers theoretically predicted Fe(η^5-N_5)$_2$, the carbon-free isoelectronic analogue of ferrocene,[59] followed by their prediction of the heavier analogues of iron bispentazole Fe(η^5-E_5)$_2$ (E = P, As, Sb).[60] Remarkably, shortly after the theoretical prediction of Fe(η^5-N_5)$_2$, Urnėžius and co-workers synthesized the first entirely inorganic sandwich compound $[Ti(\eta^5\text{-}P_5)_2]^{2-}$ (Fig. 1B) by reacting the highly reduced titanium complexes with white phosphorus at low temperature.[9] This carbon-free metallocene is highly stable toward heat and air, and can be viewed as two parallel and planar aromatic P_5^- rings sandwiching a zerovalent Ti atom.

The experimental realization of $[Ti(\eta^5\text{-}P_5)_2]^{2-}$ in turn inspired theoretical investigations on its isoelectronic analogues. In 2003, Frenking's team examined the stability and electronic properties of a series of Ti complexes $[Ti(\eta^5\text{-}E_5)_2]^{2-}$ (where E = CH, N, P, As, Sb).[11] Analyzing the computed bond dissociation energies revealed that the $[Ti(\eta^5\text{-}P_5)_2]^{2-}$ and $[Ti(\eta^5\text{-}As_5)_2]^{2-}$ complexes are intrinsically stable with reference to dissociation of one ligand. Considering the successful synthesis of $[Ti(\eta^5\text{-}P_5)_2]^{2-}$, it is highly feasible that its analogue $[Ti(\eta^5\text{-}As_5)_2]^{2-}$ could be isolated.

With these all-metal sandwiches in mind, we may expect the existence of half-sandwich clusters with Group 15 ring ligands, such as $[Fe(E_5)]^+$ (E=N, P, As). Interestingly, as Frenking and coworkers found, though the pyramidal (C_{5v}) structures can be obtained for $[Fe(E_5)]^+$ (E=N, P, As), the pyramidal structure of $[Fe(Sb_5)]^+$ collapsed during the optimization and yielded the planar D_{5h} form, which led to further discovery of the planar $[Fe(Bi5)]^+$ (Fig. 1C).[61] Note that the planar (D_{5h}) $[FeSb_5]^+$ and $[Fe(Bi5)]^+$ are the first example of a 6-π aromatic cation which has a transition metal (TM) atom in the center surrounding by an aromatic ring. These molecules are featured by strong iron–ligand π bonds which involve the d(π) atomic orbitals of the Fe center and the degenerate π orbital of the ring. The calculations predict that the cyclic ligands in Fe(η^5-Sb_5)$_2$ has a staggered conformation (D_{5d} symmetry). The contributions of covalent interaction between Fe^{2+} and two cyclo-Sb_5 ligands comes from the donation of the occupied $e_1(\pi)$ orbital of the ligands into the empty orbital of Fe^{2+} fragment.

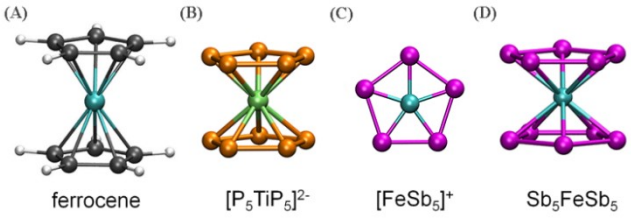

Figure 1 (A) ferrocene; (B) $[P_5TiP_5]^{2-}$; (C) $[FeSb_5]^+$; (D) Sb_5FeSb_5

The variation of transition metal, number of atoms in aromatic ring and the charge on the compound surely would inspire further studies on such type of novel compounds.

In 2009, using the Sb_4^{2-} ring [Fig. 2A], which exhibits both π- and σ-aromaticity, as building blocks, Li *et al*. theoretically investigated transition metal sandwich complexes $[Sb_4MSb_4]^{n-}$ (where M = Co, Rh, Ir, Fe, Ru, Os and n = 1 or 2) in both staggered (D_{4d} symmetry) and eclipsed (D_{4h} symmetry) configurations [Fig. 2B and 2C],[51] and revealed that energetically these complexes prefer the staggered D_{4d} geometry (Fig. 2B). The Wiberg bond indexes (WBIs) for the Sb-Sb bonds of these $[Sb_4MSb_4]^{n-}$ compounds are within 1.01 and 1.17, slightly smaller than that for the isolated Sb_4^{2-} ring (1.25), which indicates the existence of modest electron delocalization in the Sb_4^{2-} unit in these compounds. The 0.30- 0.46 WBIs for the M-Sb bonds suggest that the interactions between the central transition metal and the Sb_4^{2-} rings are partially covalent and partially ionic. The same as its isoelectronic As_4^{2-} and P_4^{2-} species,[62,63] the Sb_4^{2-} fragment in the sandwich compounds has three π molecular orbitals, namely the degenerated HOMOs and the HOMO-2 (Fig. 2D), these 6 π electrons result in π aromaticity of Sb_4^{2-}. Moreover, the cyclic σ symmetrical molecular orbitals, HOMO-3 and HOMO-7 (Fig. 2D) induce σ ring current. The calculated negative NICS(0) and NICS(1) values[64,65] of the evaluated compounds $[Sb_4MSb_4]^{n-}$ also confirm their aromatic characters. They also examined the effect of the central transition metal to the aromaticity in these compounds, and concluded that electron delocalization gradually decreases with increasing the atomic number of the transition metals. Some sandwich-type dinuclear complexes were also studied theoretically.[66]

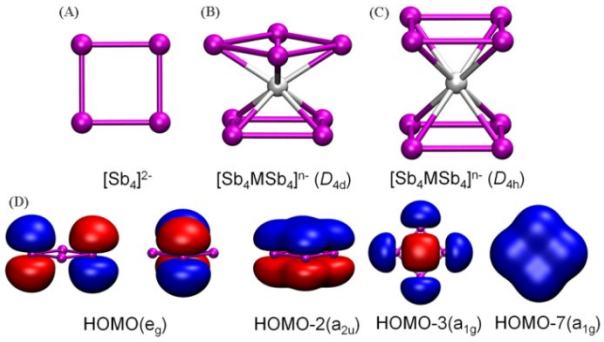

Figure 2 (A) Sb_4^{2-}; (B) $[Sb_4MSb_4]^{n-}$ with D_{4d} symmetry; (C) $[Sb_4MSb_4]^{n-}$ with D_{4h} symmetry (M = Co, Rh, Ir, Fe, Ru, Os and n = 1 or 2); (D) three π and two σ symmetrical molecular orbitals. Reproduced from ref. 51.

Similarly, many other all-metal sandwich compounds such as $[Sb_5TiSb_5]^{2-}$, $[Sb_4FeSb_4]^{2-}$ and $[Al_4TiAl_4]^{2-}$, have been theoretically predicted.[11, 24, 51, 67-71] However, no such kind of all-metal sandwich complexes, in which a transition metal atom or sheet is jammed between two aromatic metal rings, have been practically isolated until Sun and co-workers successfully isolated the first all-metal aromatic sandwich complex, $[Sb_3Au_3Sb_3]^{3-}$, as K([2.2.2]crypt)$^+$salt in 2015.[72] The X-ray diffraction revealed that $[Sb_3Au_3Sb_3]^{3-}$ adopts an approximate D_{3h} symmetry (Fig. 3A), in which the Au_3 and Sb_3 rings are nearly equilateral and a mononuclear Au_3 sheet is sandwiched between two layers of Sb_3 metal atoms. Two *cyclic*-Sb_3 fragments in $[Sb_3Au_3Sb_3]^{3-}$ accommodate or bind Au_3 ring favorably through Au-Sb interactions. Intramolecular electron transfer occurs between Au_3 and Sb_3 in this cluster, where the two Sb_3 units serve as the electron donor and the Au_3 sheet as an electron acceptor. DFT computations revealed that HOMOs and HOMO-3, which are basically attributed to two cyclic-Sb_3 fragments, have dominant aromatic character (Fig. 3E). Interaction between Au_3 and two cyclic-Sb_3 units is achieved via the donation and back donation processes [Fig. 3B-D], which hold the whole sandwich compound together steadily. Consequently, each Sb_3 unit effectively has three 3c-2e orbitals occupied by six

electrons derived from Sb s and p orbitals,[68,73,74] which results in a special aromaticity. The aromaticity character of $[Sb_3Au_3Sb_3]^{3-}$ was also confirmed by the theoretical aromaticity probe, NICS.[64,65] The calculated $NICS(1)_{ZZ}$ [75] value of -23.13 ppm for each cyclic-Sb_3 unit is almost comparable with benzene ($NICS(1)_{ZZ}$ = -29.87 ppm) at the same theoretical level, which strongly supports the high aromaticity this novel triangular cluster, $[Sb_3Au_3Sb_3]^{3-}$.

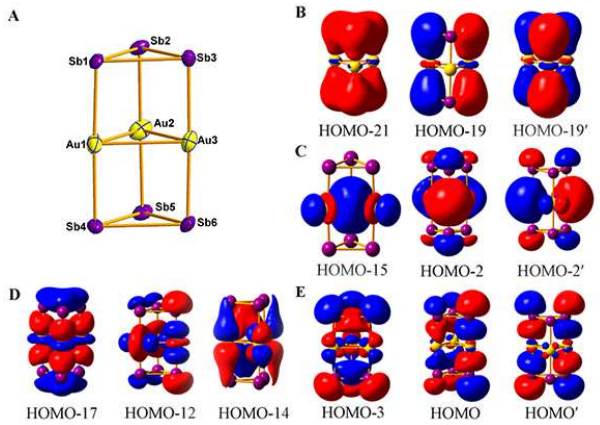

Figure 3 Some related molecule orbitals and the thermal ellipsoid plot of the molecular cluster anion $[Sb_3Au_3Sb_3]^{3-}$ (drawn at 50% probability). Reproduced from ref. 72.

Kirk, Jenkins and co-workers[76] performed Quantum Theory of Atoms In Molecules (QTAIM) and stress tensor analysis of $[Sb_3Au_3Sb_3]^{3-}$. Their findings are consistent with previous evaluation of its aromatic character, and showed that the bond critical points (BCPs) of Sb-Au and Sb-Sb possess metallicity.

Li *et al.* performed further theoretical analysis on $[Sb_3Au_3Sb_3]^{3-}$.[77] By comparing the electronic structures of $[Sb_3Au_3Sb_3]^{3-}$ and its congeners, $[X_3Au_3X_3]^{3-}$ (X = N, P, As, Sn, Bi, Uup) as well as $[X_3MX_3]^{3-}$ (M, X = Cu, As; Ag, Bi; Au, Sb; Rg, Uup), they found that there might exist other stable $[A_pM_pA_p]^{x-}$ (M = transition metals, A = main group elements, p = 3, 4, 5, …) sandwich ions and oligomers (Fig. 4). The intralayer and interlayer chemical bonding interaction in this system was determined by the interlayer (p-d-p)σ interactions between the vertical Au 5d6s hybrid orbitals of Au3 and Sb 5pπ orbitals of the Sb_3 rings. The calculated results revealed that these sandwich compounds can form stable extended systems under appropriate experimental conditions.

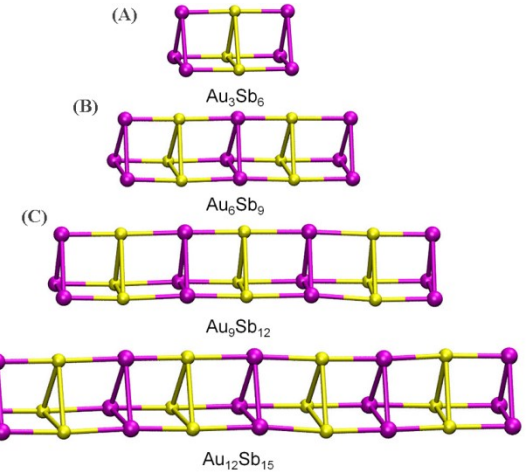

Figure 4 Optimized structures of $[Sb_3–(Au_3Sb_3)_n]^{3-}$ (n = 1, 2, 3, 4) oligomers. Reproduced from ref. 77.

Researchers also explored the possibility to have a central metal ring with more than three atoms in the all-metal sandwich complexes. Along this line, Tian *et al.* computationally designed $[Sb_4Au_4Sb_4]^{2-}$(Fig. 5), which can be formally described as $[Sb_4]^{+}[Au_4]^{4-}[Sb_4]^{+}$.[78,79] Each $[Sb_4]^{+}$ ligand features a three-fold (π and σ) aromatic system with 22 delocalized electrons, and there are remarkable Sb to Au donation and significant Au to Sb back donation. Such a phenomenon redistributes electrons from the three layers, $Sb_4/Au_4/Sb_4$, to the interlayer edges, successfully resulting in four Sb-Au-Sb 3c-2e σ bonds, which help stabilize this $[Sb_4Au_4Sb_4]^{2-}$ sandwich complex. Noteworthy, both the $[Sb_4]^{+}$ units are shown to be of σ-radial, σ-tangential and π-aromaticity, whose 22 valence electrons are fully delocalized in three-fold nature, indicating a very unusual and complicated chemical bonding system.

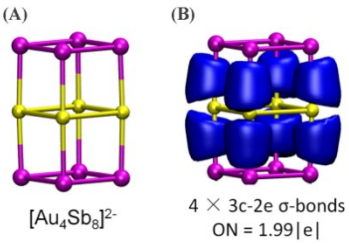

Figure 5 Optimized D_{4h} structure of $[Au_4Sb_8]^{2-}$, along with its four 3c-2e σ bonds Reproduced from ref. 79.

Recently, Zhu *et al.* theoretically predicted some all-metal clusters, $[Sb_3Au_3Sb_3]^{3-}$ and its analogues, $[Sb_nAu_nSb_n]^{m}$ (n = 3, 4, 5, 6,; m = -3, -2, -1, -2).[80] According to their analysis, these corresponding sandwich-like complexes hold tube aromaticty. The complete aromatic character of cyclic-Sb_4 approves with the results achieved in the recent studies.[72]

3. All-metal Sb clusters with σ-aromaticity

The σ-aromaticity concept was previously used to rationalize the enhanced stability of alkali and alkaline earth metal clusters.[81] Recently, σ-aromaticity was extended into the burgeoning field of intermetallic clusters. In the early examples, these intermetallic compounds, with σ-aromaticity in a solid state, always contain two delocalized electrons satisfying the 4n+2 rule (n = 0), such as in the case of Pd_3^{+}, Au_3^{+}, and $TiSn_2$ clusters.[82-84]

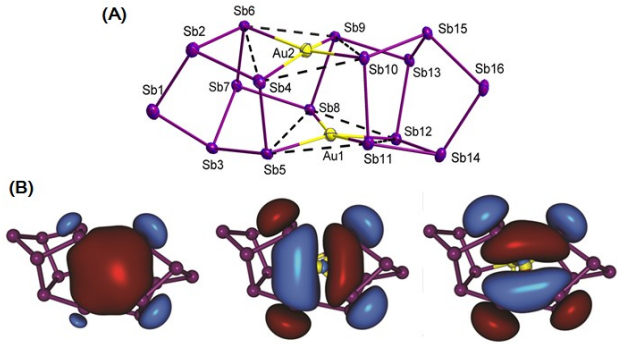

Figure 6 Thermal ellipsoid plot of the molecular cluster anion $[Au_2Sb_{16}]^{4-}$. Delocalized chemical bonding elements deciphered for the complex $[Au_2Sb_{16}]^{4-}$. Six 5c-2e delocalized σ bonds. Reproduced from ref. 85.

The situation changed in 2016 when the solid state cluster, $[Au_2Sb_{16}]^{4-}$, was isolated. This cluster consists of two $AuSb_4$ all-metal σ-aromatic units, each containing six delocalized electrons.[85] It was the first example in the family of storable aromatic all-metal clusters that satisfies the 4n+2 rule (n = 1). Till now, $[Au_2Sb_{16}]^{4-}$ is the largest unfragmented intermetallic cluster Sb_n in solid state due to the unique σ aromatic stabilization through quenching with two Au atoms, which demonstrates the efficacy of σ-aromaticity concept in the concerned area of solid-state clusters.

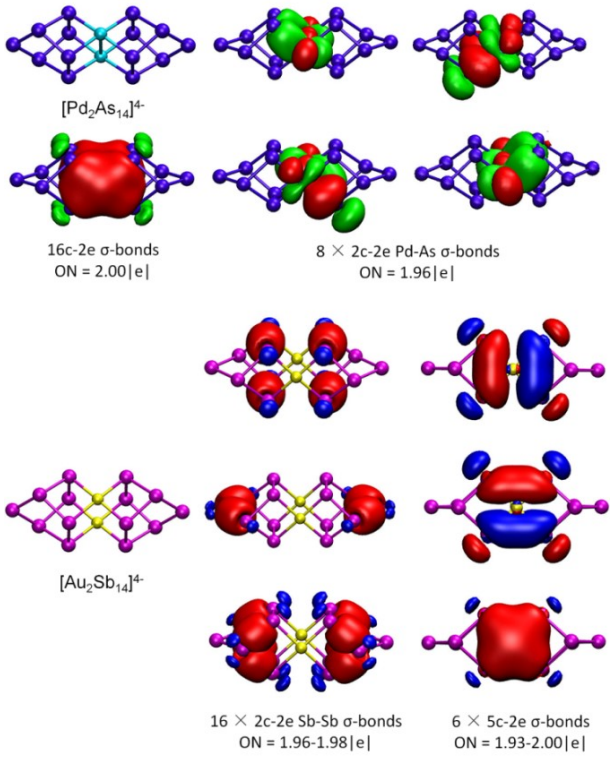

Figure 7 Optimized D_{2h} structure of $[Pd_2As_{14}]^{4-}$ (top left) and $[Au_2Sb_{14}]^{4-}$ (bottom left), along with their peculiar bonding patterns. Reproduced from ref. 88.

In the $[Au_2Sb_{16}]^{4-}$ complex, two Au atoms are situated on the surface, offering unusual geometric shapes and complicated electronic structure. As shown in Fig. 6, two Au atoms inlay on the surface of the Sb_{16} polyanion framework and each Au atom in $[Au_2Sb_{16}]^{4-}$ is coordinated by four Sb atoms. To elucidate the electronic structure of $[Au_2Sb_{16}]^{4-}$, Popov et al. performed the chemical bonding analysis using the Adaptive natural density partitioning (AdNDP) method.[86] According their analysis, there are 10 d-type electron lone pairs collectively on both Au atoms, 16 s-type lone pairs on 16 Sb atoms, two p-type lone pairs on two exterior Sb1 and Sb16 atoms, and 19 classical two-center-two-electron (2c-2e) Sb-Sb σ-bonds, and the joint force of all these bonds is responsible for the direct interactions among the Sb atoms leading to the unique structure of $[Au_2Sb_{16}]^{4-}$ (Fig. 6A). Interestingly, no Sb-Sb or Au-Sb classical 2c-2e σ-bond on any $AuSb_4$ unit was found, instead, AdNDP analysis showed that 12 electrons take part in delocalized bonding, and there are three five-center two-electron (5c-2e) σ-bonds among quasi-planar $AuSb_4$ blocks. Indeed, Au contributes its 6s atomic orbitals in the completely bonding orbital. Basically, among these three 5c-2e bonds (Fig. 6B), one is completely bonding, while the other two possess one nodal plane (mutually perpendicular) with n = 1 in accordance with the 4n+2 rule, which is closely resemble the classical σ-aromatic bonds found in the gas-phase B_7^- cluster.[87] In particular, the analysis of electronic multicenter indices (I_{ring} and MCIs) showed that the delocalization of electrons appeared through a zigzag pattern. They also compared $[Au_2Sb_{16}]^{4-}$ with two aromatic model systems, $[AuSb_4H_8]^-$ and $[Sb_4H_4]^{2-}$. The marked resemblance in the electronic structures and geometries of the $AuSb_4$ fragments of the model clusters and the synthesized complex $[Au_2Sb_{16}]^{4-}$clearly confirms the σ-aromatic character of $[Au_2Sb_{16}]^{4-}$ cluster.

The fascinating structure and bonding of $[Au_2Sb_{16}]^{4-}$ inspired Zhai *et al*. to design its analogue, $[Au_2Sb_{14}]^{4-}$ with special σ-aromaticity.[88] They further investigated the isolated cluster $[Pd_2As_{14}]^{4-}$ by DFT calculations. As shown in Fig. 7, two Sb_7 cages with C_{2v} symmetry are held by one Au dimer, leading to a large cage $[Au_2Sb_{14}]^{4-}$ with D_{2h} symmetry via six 5c-2e σ-bonds. This is similar to the previously reported $[Au_2Sb_{16}]^{4-}$. In contrast, the $[Pd_2As_{14}]^{4-}$ possesses four 2c-2e σ-bonds and one 16c-2e σ-bonds in each slightly distorted square-planar $PdAs_4$ units. The structure of the $[Pd_2As_{14}]^{4-}$ cluster has been characterized in solid by Reber *et al*.[89] Thus, the special σ-aromaticity plays an important role in forming this kind of large intermetallic cages.

Very recently, Xia and Zhu *et al.* isolated a peculiar unsaturated Se-containing three-membered ring with prominent σ-aromaticity.[90] By incorporating a transition metal fragment, σ-aromaticity succeeded in overwhelming the ring strain of selenirene and pentalene frameworks.

4. Unique π-antiaromaticity in Sb4 cluster

The concept of antiaromaticity was introduced by Breslow in 1965, usually referring to monocyclic organic systems with 4n π-electrons.[4,5] This concept has been extended to some inorganic molecules along with an improved quantum-mechanical understanding. The observation of $Li_3Al_4^{4-}$ in the gas phase ushers in a new era, the field of all-metal π-antiaromatic molecules.[25]

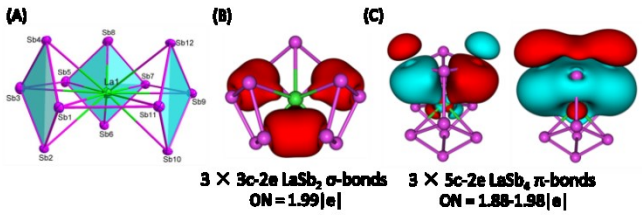

Figure 8 Take $[La(\eta^4\text{-}Sb_4)_3]^{3-}$ as an example here. (A) The structure of $[La(\eta^4\text{-}Sb_4)_3]^{3-}$, (B) 3c-2e σ bonds and (C) the unique 5c-2e π bonds. Reproduced from ref. 91.

The synthesis and characterization of solid-state compounds involving anti-aromatic units is practically much more stimulating because of their high reactivity and low stability. Min *et al.* reported first time a series of all-metal anti-aromatic anions in the solid state, $[Ln(\eta^4\text{-}Sb_4)_3]^{3-}$(where, Ln = Lu, Er, Ho, Y, La,) as their K([2.2.2]crypt) salts, and characterized their structures by single crystal XRD (Fig. 8A). [91] According to the electron counting rule and chemical bonding analysis, the cluster $[Ln(\eta^4\text{-}Sb_4)_3]^{3-}$ contains three π-antiaromatic Sb_4 units, but is stabilized by the intramolecular interactions within the Sb_4 π-antiaromatic subunits.

The deviation from planarity and the uniform bond lengths suggest distinctive electronic structures in the cyclic Sb_4 fragments. The AdNDP analyses identified 12 lone pairs of s-type electrons on 12 Sb atoms, 12 classical 2c-2e Sb-Sb σ bonds (four on each units of cyclic Sb_4 unit, which are actually accountable for the interactions between the three cyclic Sb_4 units (Sb9–Sb12, Sb5–Sb8 and Sb1–Sb4), three 3c-2e σ bonds (Sb1-La-Sb11, Sb3-La-Sb5, and Sb7-La-Sb9 as shown in Fig. 8B) which bond the three distinct cyclic Sb_4 fragments in the equatorial plane, and six 5c-2e π bonds on the three $LaSb_4$ units (Fig. 8C). These two 5c-2e π bonds are analogous with the previously discussed 4c-2e π bonds in the neutral Sb_4 cluster, and the four π electrons herein suggest the π anti-aromatic character of Sb_4 subunits. In short, the electron-counting rule and the AdNDP analyses both suggest that the compound $[Ln(\eta^4\text{-}Sb_4)_3]^{3-}$ holds three π anti-aromatic Sb_4 units. A key question here is why such unstable anti-aromatic fragments exist in Ln-type anions. Basically, it is the strong bonding among the anti-aromatic cyclic Sb_4 fragments and Ln that stabilizes the entire $[Ln(\eta^4\text{-}Sb_4)_3]^{3-}$ compound.

The electron count and effective oxidation-state analysis showed that the Ln atom holds a positive 3^+ charge in all $[Ln(\eta^4\text{-}Sb_4)_3]^{3-}$clusters, which results in a negative 2^- charge on each cyclic Sb_4 unit.[92, 93] Note that an aromatic Sb_4^{2-} unit in the gas phase having a square-planar geometry and 6π electrons was observed before. [94] However, the bonding pattern in Sb_4^{2-} unit and that in the Sb_4 fragment of $[Ln(\eta^4\text{-}Sb_4)_3]^{3-}$ differ significantly because of the strong interactions between the central Ln atom and the Sb_4 units in the latter case. More precisely, noticeable equatorial Sb-Sb interaction exists among the nearby Sb_4 fragments, in addition to the central Ln atom and the cyclic Sb_4 units, through 3c-2e σ bonds in $[Ln(\eta^4\text{-}Sb_4)_3]^{3-}$ **(**Fig. 8B). Indeed, almost two electrons from each Sb_4 block contribute to the establishment of the 3c-2e intra-cluster equatorial bonds. Hence individual four electrons remain for the π-network on the cyclic Sb_4 fragment. So, the rhombic distortion structure of Sb_4 blocks can be thought as a direct concern of its anti-aromaticity.

The electronic multicenter indices[45, 47] exposed that the Sb_4 units are more alike to cyclobutadiene as compared to cyclobutane. Actually, the interaction of the three cyclic Sb_4^{2-} units towards the Ln^{3+} ion considerably depresses the aromaticity of the Sb_4 moieties, this situation is rather similar to cyclobutadiene, an anti-aromatic counterpart.

These $[Ln(\eta^4\text{-}Sb_4)_3]^{3-}$compounds exemplify the first Ln/main group all-metal anionic clusters. Such type of clusters have not ever been separated before in the solid phase, thus opened a new pathway to synthesize unique bimetallic lanthanide clusters, and will inspire further inquiries of antiaromaticity both in materials science and inorganic chemistry.

5. Conclusions and Perspectives

This Review summarizes recent breakthroughs in the synthesis and theoretical understanding of a series of novel Sb_n clusters and even group 15 clusters featuring π-aromaticity, σ-aromaticity, and π-antiaromaticity. Aromaticity and antiaromaticity concepts can greatly enrich our understanding of the stability, structure, and chemical bonding of main group clusters and related compounds, and have a great potential to bring us many more enticing cluster compounds with unique structures and properties. No doubt, a great diversity of aromatic cluster compounds beyond what reviewed here will be synthesized by the ingenuity of experimental chemists, and theoreticians will continue to provide insightful analysis into the unique structure and chemical bonding, and offer experimentalists interesting targets to synthesize. We also strongly believe that these concepts will further help us rationalize some complicated properties in other areas of materials science. The over 150-year-old aromaticity concept will continue to shine!

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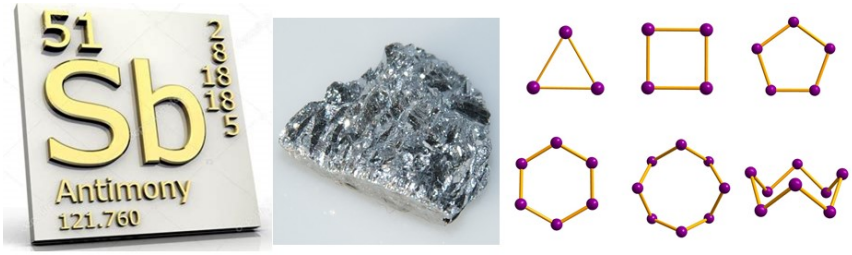

Lei-Jiao Li, Basharat Ali, Zhongfang Chen* and Zhong-Ming Sun*

The Sb_n clusters feature unique chemical bonding, fascinating structures, and special stabilities that can be well rationalized by aromaticity or antiaromaticity.

