

Antiaromaticity

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All-Metal Antiaromaticity in Sb₄-Type Lanthanocene AnionsXue Min[†], Ivan A. Popov[†], Fu-Xing Pan, Lei-Jiao Li, Eduard Matito, Zhong-Ming Sun,*
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Abstract: Antiaromaticity, as introduced in 1965, usually refers to monocyclic systems with $4n$ π electrons. This concept was extended to all-metal molecules after the observation of Li_3Al_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, $[\text{Ln}(\eta^4\text{-Sb}_4)_3]^{3-}$ ($\text{Ln} = \text{La}, \text{Y}, \text{Ho}, \text{Er}, \text{Lu}$), which were isolated as the $\text{K}([2.2.2]\text{crypt})$ salts and identified by single-crystal X-ray diffraction. Based on the results obtained from the chemical bonding analysis, multi-center 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 π -antiaromatic Sb_4 fragments. This complex represents the first locally π -antiaromatic all-metal system in the solid state, which is stabilized by interactions of the three π -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 π 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 π 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-diazadiboretiidine ($\text{B}_2\text{N}_2\text{H}_4$) 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 diazadiboretiidines have been reported.^[6] Whereas the cyclic B_2N_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 π 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-} ($\text{E} = \text{Si}, \text{Sn}, \text{Pb}$), Pn_5^- , Pn_4^{2-} ($\text{Pn} = \text{P}, \text{As}, \text{Sb}, \text{Bi}$), and X_4^{2+} ($\text{X} = \text{S}, \text{Se}, \text{Te}$), 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 π electrons.^[11a]

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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 π -antiaromatic building blocks. Recently, we reported an all-metal aromatic sandwich Au-Sb cluster.^[13] In this context, delocalized π 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-} ^[14] through stabilization by certain metal cations. Moreover, Dehnen and co-workers have synthesized a handful of ternary intermetallic cage-like anions, in which lanthanide atoms are encapsulated by mixed Group 13/15 or 14/15 cages.^[15] Their investigations show a delocalization of lone pairs in main-group metal frameworks toward the empty d_2 orbital of 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 K_5Sb_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**), Y (**2**), Ho (**3**), Er (**4**), or Lu (**5**)), which are governed by antiaromaticity. Quantum-chemical calculations indeed indicated that there is a redistribution of the valence electrons from the *cyclo*- Sb_4 units to Ln^{3+} .

Compounds **1–5**, $[\text{Ln}(\eta^4\text{-Sb}_4)_3]^{3-}$, feature three all-metal π -antiaromatic Sb_4 rhombic units as coordination ligands, which are all very air-sensitive and have quasi- D_{3h} symmetry, as shown in Figure 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*- Sb_4 units; this structure type is similar to lanthanocene, LnCp_3 ($\text{Cp} = \text{cyclopentadiene}$), except that there are equatorial interactions between adjacent *cyclo*- Sb_4 units (average Sb-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 isostructural 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. The data for the other compounds can be found in the Supporting Information.

Among the three $\eta^4\text{-Sb}_4$ units or the twelve Sb atoms around the La atom (Figure 1), there are two types of La-Sb interactions: six to Sb atoms in equatorial positions (between La and Sb1, Sb3, Sb5, Sb7, Sb9, and Sb11), 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 ($\text{R} = \text{organic group}$)^[16] have been described. Molecular all-metal rare-earth polyantimonide clusters have never been synthesized, whereas the analogous transition-metal polyan-

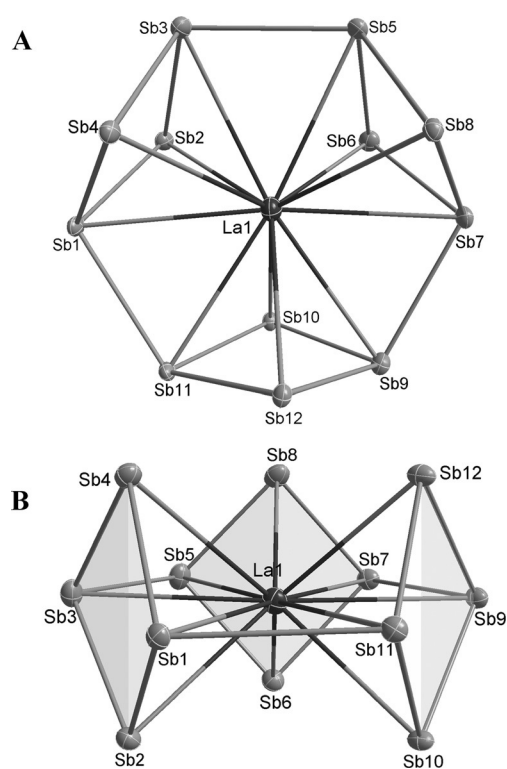


Figure 1. The structure of $[\text{La}(\eta^4\text{-Sb}_4)_3]^{3-}$ (**1**). Thermal ellipsoids set at 50% probability. A) Top view of the central projection. B) Side view. Selected bond ranges: Bonds between La and equatorial Sb atoms: 3.4338(5)–3.4735(5) Å; bonds between La and non-equatorial Sb atoms: 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.

timonide clusters have been intensively investigated.^[17] As a result of the lanthanide contraction, the average Ln-Sb distances decrease significantly across the Ho, Er, and Lu analogues (see the Supporting Information, Table S2 and Figure S2). Furthermore, the contraction effect is also reflected in the dihedral angles in the *cyclo*- Sb_4 units from La to Lu (Table S3, Figure S3). The average Sb-Sb bond lengths (2.819 Å) within the *cyclo*- Sb_4 units are comparable among all five complexes, and they are slightly longer than those in previously isolated Sb_4^{2-} (2.750 Å).^[14] Three-dimensional views of the compounds are shown in Figure 2.

The uniform bond lengths and the deviation from planarity imply unique electronic structures in the *cyclo*- Sb_4 units. To improve our understanding of the structure and bonding in the new $[\text{Ln}(\eta^4\text{-Sb}_4)_3]^{3-}$ species, we performed chemical bonding analyses using the adaptive natural density partitioning (AdNDP) method.^[18] Detailed AdNDP results can be found in the Supporting Information. In brief, the AdNDP analyses revealed twelve s-type lone pairs on the twelve Sb atoms (Figure 3A), twelve classical 2c-2e Sb-Sb σ bonds (4 on each *cyclo*- Sb_4 unit; Figure 3B), which are responsible for the bonding within the three separated *cyclo*- Sb_4 blocks (Sb1–Sb4, Sb5–Sb8, and Sb9–Sb12), three 3c-2e σ bonds, which are responsible for the bonding between the three separate *cyclo*- Sb_4 units in the equatorial plane, as well

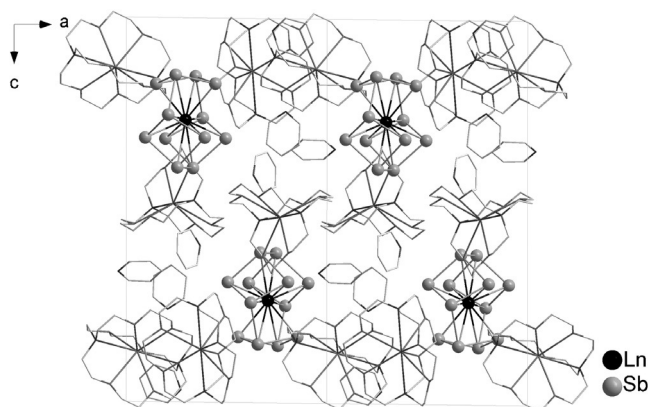


Figure 2. $[\text{K}([2.2.2]\text{crypt})]_3[\text{Ln}(\eta^4\text{-Sb}_4)_3] \cdot 4\text{py}$ ($\text{Ln} = \text{La}, \text{Y}, \text{Ho}, \text{Er}, \text{Lu}$) viewed down the b axis. Hydrogen atoms were omitted for clarity.

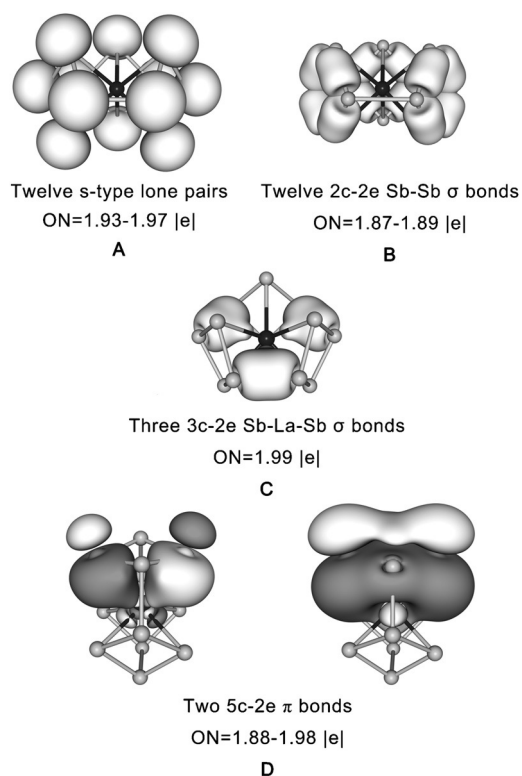


Figure 3. Chemical bonding analysis by the AdNDP method at the Def2-SVPD level of theory. A) The twelve s-type lone pairs (1c-2e bonds) on twelve Sb atoms (1 per Sb atom), shown superimposed onto the molecular framework. B) The twelve 2c-2e Sb-Sb σ bonds, shown superimposed onto the molecular framework. C) The three 3c-2e σ bonds, shown superimposed onto the molecular framework. D) Two 5c-2e π bonds on one *cyclo-Sb*₄ unit. The four other 5c-2e π bonds were omitted for clarity. ON stands for occupation number and is equal to 2.0 |e| in an ideal case.

as for the interaction of La with the equatorial Sb atoms (La/Sb1/Sb11, La/Sb3/Sb5, and La/Sb7/Sb9, Figure 3C), and six 5c-2e π bonds on the three LaSb₄ fragments (two 5c-2e π bonds on each fragment are shown in Figure 3D).

The two 5c-2e π bonds on each Sb₄ fragment are quite similar to the two 4c-2e π bonds in the distorted rectangular

structure of a neutral Sb₄ 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 $[\text{Ln}(\eta^4\text{-Sb}_4)_3]^{3-}$ cluster contains three π -antiaromatic Sb₄ 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 $[\text{Ln}(\eta^4\text{-Sb}_4)_3]^{3-}$ complex.

A simple electron count reveals that the Ln atom possesses a positive charge of 3+ in the ionic limit in all the $[\text{Ln}(\eta^4\text{-Sb}_4)_3]^{3-}$ 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] (see the Supporting Information for details). An aromatic Sb₄²⁻ species with 6 π electrons and a square-planar structure has previously been isolated.^[20] However, the bonding situation in the *cyclo-Sb*₄ units in the $[\text{Ln}(\eta^4\text{-Sb}_4)_3]^{3-}$ cluster is different from that in an isolated Sb₄²⁻ dianion owing to the interactions between the Sb₄ 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 $[\text{Ln}(\eta^4\text{-Sb}_4)_3]^{3-}$ (Figure 3C). 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 Sb₄ units can be considered as a direct consequence of its antiaromaticity. We believe that the local π antiaromaticity of the Sb₄ units is also consistent with the very high air sensitivity and reactivity of all of the $[\text{K}([2.2.2]\text{crypt})]_3[\text{Ln}(\eta^4\text{-Sb}_4)_3] \cdot 4\text{py}$ compounds.

Additional information on the antiaromaticity of the *cyclo-Sb*₄ units could potentially be obtained on the basis of nucleus independent chemical shift (NICS) indices.^[21] However, such an analysis by Tsipis^[22] showed that the Sb₄²⁻ 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_{ring} and MCI),^[23,24] which were previously shown to give excellent results for organic,^[23-25] all-metal,^[26] and inorganic^[27] compounds, providing aromaticity trends that are superior to those furnished by NICS.^[28] The multicenter calculations showed that the Sb₄ blocks are more similar to cyclobutadiene than to cyclobutane (see the Supporting Information for further details). In fact, coordination of the three Sb₄²⁻ moieties with the La³⁺ ion drastically reduces the aromaticity of the Sb₄ 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, $[\text{Ln}(\eta^4\text{-Sb}_4)_3]^{3-}$ ($\text{Ln} = \text{La}, \text{Y}, \text{Ho}, \text{Er}, \text{Lu}$), have been synthesized and structurally identified; the Ln³⁺ ions are facially coordinated by three antiaromatic *cyclo-Sb*₄ units. Chemical bonding analyses by AdNDP of the $[\text{Ln}(\eta^4\text{-Sb}_4)_3]^{3-}$ complexes showed that the Sb₄ building blocks feature four π electrons and are thus antiaromatic according to Breslow's

$4n$ rule. The calculated multicenter indices reveal strong resemblance with cyclobutadiene,^[29] thus confirming the antiaromatic character of the Sb_4 fragments. The stability of the $[\text{Ln}(\eta^4\text{-Sb}_4)_3]^{3-}$ complexes was found to be due to interactions within the Sb_4 units and additional interactions between the *cyclo*- Sb_4 units and the central lanthanide atom. The $[\text{Ln}(\eta^4\text{-Sb}_4)_3]^{3-}$ 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.

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