

Aromaticity

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Peculiar All-Metal σ -Aromaticity of the $[\text{Au}_2\text{Sb}_{16}]^{4-}$ Anion in the Solid StateIvan A. Popov⁺, Fu-Xing Pan⁺, Xue-Rui You, Lei-Jiao Li, Eduard Matito, Chao Liu, Hua-Jin Zhai, Zhong-Ming Sun,* and Alexander I. Boldyrev*

Abstract: Gas-phase clusters are deemed to be σ -aromatic when they satisfy the $4n + 2$ rule of aromaticity for delocalized σ 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 $[\text{K}([2.2.2]\text{crypt})]^+$ salt, featuring a $[\text{Au}_2\text{Sb}_{16}]^{4-}$ cluster core possessing two all-metal aromatic AuSb_4 fragments with six delocalized σ electrons each ($n = 1$). This discovery pushes the boundaries of the original idea of Kekulé and firmly establishes the usefulness of the σ -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 π aromaticity/antiaromaticity were primarily used to explain chemical bonding in organic compounds. Today, these terms are well used for 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 co-workers reported^[3] the synthesis of $\text{Na}_2[(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)_2\text{C}_6\text{H}_3]\text{Ga}_3$ with two π electrons delocalized over the three gallium atoms that make the system π -aromatic according to the Hückel rule. Recently, the first solid-state all-metal π -antiaromatic compounds $[\text{Ln}(\eta^4\text{-Sb}_4)]_3^{3-}$ ($\text{Ln} = \text{La}, \text{Y}, \text{Ho}, \text{Er}, \text{Lu}$) were synthesized and characterized.^[4] The $[\text{U}@\text{Bi}_{12}]^{3-}$ 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 σ -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 σ -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 σ -aromatic fragments involving six delocalized electrons each. Hence, the 6- σ -electron aromatic fragments found in the $[\text{Au}_2\text{Sb}_{16}]^{4-}$ cluster in this study expand the family of storable aromatic metal clusters thus solidifying usefulness of the σ -aromaticity concept in the solid state.

The title complex $[\text{Au}_2\text{Sb}_{16}]^{4-}$ (**1**), crystallizes in the form of $[\text{K}([2.2.2]\text{crypt})]_4 \cdot 4\text{en}$ (Figure S1 and Table S1), was isolated from an ethylenediamine (en) solution of K_3Sb_7 , $\text{Au}(\text{PPh}_3)\text{Ph}$, and 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo-[8.8.8]hexacosane ($[2.2.2]\text{crypt}$; experimental details can be found in the Supporting Information). As shown in Figure 1, 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 82.35–105.69° for Au1 and 82.67–107.96° 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 1). The Au–Sb bond lengths (2.69 ± 0.02 Å) span a very narrow range, thus underlining the importance of Au–Sb interactions

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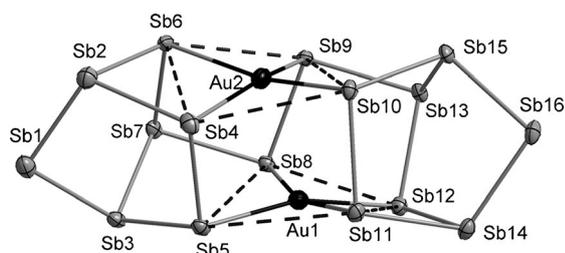


Figure 1. Thermal ellipsoid plot of complex **1** (drawn at 50% probability). Selected bond lengths (Å) and angles (°): Au1–Sb5 2.6745(16), Au1–Sb8 2.6835(15), Au1–Sb11 2.6736(15), Au1–Sb12 2.6784(17), Au2–Sb4 2.7060(17), Au2–Sb6 2.6748(15), Au2–Sb9 2.6864(17), Au2–Sb10 2.6683(14), Sb8–Sb9 2.8193(17); Sb5–Au1–Sb11 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.

within the two AuSb₄ units, and the bonds are slightly longer than those in recently reported [Sb₃Au₃Sb₃]³⁻ (2.60 Å in average),^[15] but shorter than those in some organometallic compounds such as (1,8-naphthalenediyl)₂(Ph₂Sb)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 Sb₁₆ species in **1** represents the largest unfragmented Sb_{*n*} polyanion known that was isolated from solution (Figure S2). 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 S3). 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 (Table S2).

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] Full details of the AdNDP calculations can be found in the Supporting Information. 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 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 S4). 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 2) look like

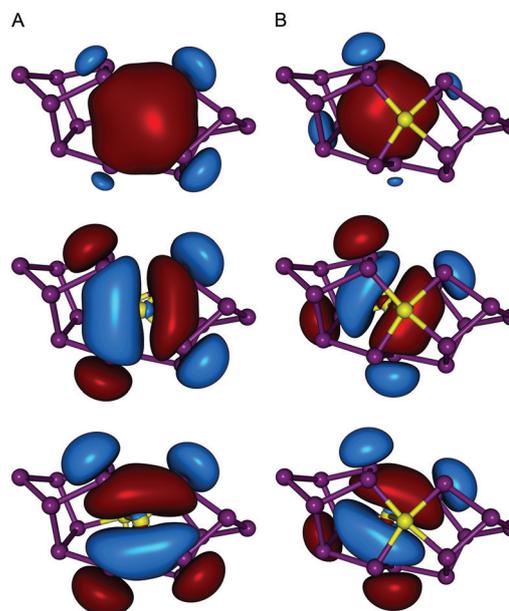


Figure 2. Delocalized chemical bonding elements deciphered for complex **1**. Six 5c-2e delocalized σ bonds with ON = 1.86–1.99 |*e*| found at the A) upper AuSb₄ (Au1–Sb5–Sb8–Sb11–Sb12) and B) lower AuSb₄ (Au2–Sb4–Sb6–Sb9–Sb10) fragments.

classical σ-aromatic bonds found for gas-phase clusters (e.g., in the B₇⁻ cluster^[20]): one completely bonding and two bonds possessing one nodal plane (mutually perpendicular) with *n* = 1 according to the 4*n* + 2 rule. A simple orbital diagram schematically explaining the observed 5c-2e bonds is shown in Figure S6.

Importantly, this observation is in concordance with the Au–Sb bond equalization in the two AuSb₄ fragments that supports the aromaticity pattern. However, as seen from the geometry of complex **1**, these two AuSb₄ 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, [AuSb₄H₈]⁻ and [Sb₄H₈]²⁻. The first cluster (Figure S7) has the same number of electrons in the AuSb₄ 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 S9). Pronounced similarity in the geometries and electronic structures of the AuSb₄ fragment of the experimental com-

plex **1** and the model clusters clearly confirms the σ -aromaticity pattern in these systems (see the Supporting Information for further details). 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 S7–S10).

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_{ring} and MCIs),^[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 $[AuSb_4H_8]^-$ 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 (4.2×10^{-3} and 8.3×10^{-3} , respectively) are not as large as in the $[Sb_4H_8]^{2-}$ model (40×10^{-3}), but the values cannot be overlooked and indicate an incipient aromatic character.

In summary, the $[Au_2Sb_{16}]^{4-}$ (**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 σ -aromatic stabilization through quenching with two Au atoms, which participate in delocalized bonding to form two quasi-planar $AuSb_4$ σ -aromatic fragments. Data obtained from the analysis of the electronic structures of **1**, and the model clusters $[AuSb_4H_8]^-$ and $[Sb_4H_8]^{2-}$ as well as the electronic indices of these systems proved that the two quasi-planar $AuSb_4$ moieties in **1** are indeed σ -aromatic due to the interaction of the Au atom with four neighboring Sb atoms in a delocalized manner. Thus, the $[Au_2Sb_{16}]^{4-}$ anion is the first solid-state all-metal σ -aromatic cluster that possesses two peculiar σ -aromatic $AuSb_4$ fragments featuring six delocalized σ 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.

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- [1] A. Kekulé, *Bull. Soc. Chim.* **1865**, *3*, 98–110.
- [2] G. Merino, M. Solá, *Phys. Chem. Chem. Phys.* **2016**, *18*, 11587–11588.
- [3] X.-W. Li, W. T. Pennington, G. H. Robinson, *J. Am. Chem. Soc.* **1995**, *117*, 7578–7579.
- [4] X. Min, I. A. Popov, F.-X. Pan, L.-J. Li, E. Matito, Z.-M. Sun, L. S. Wang, A. I. Boldyrev, *Angew. Chem. Int. Ed.* **2016**, *55*, 5531–5535; *Angew. Chem.* **2016**, *128*, 5621–5625.
- [5] N. Lichtenberger, R. J. Wilson, A. R. Eulenstein, W. Massa, R. Clérac, F. Weigend, S. Dehnen, *J. Am. Chem. Soc.* **2016**, *138*, 9033–9036.
- [6] X. Li, A. E. Kuznetsov, H. F. Zhang, A. I. Boldyrev, L. S. Wang, *Science* **2001**, *291*, 859–861.
- [7] A. N. Alexandrova, A. I. Boldyrev, *J. Phys. Chem. A* **2003**, *107*, 554–560.
- [8] A. P. Sergeeva, I. A. Popov, Z. A. Piazza, W.-L. Li, C. Romanescu, L. S. Wang, A. I. Boldyrev, *Acc. Chem. Res.* **2014**, *47*, 1349–1358.
- [9] “Chemical Bonding in Inorganic Aromatic Compounds”: I. A. Popov, A. I. Boldyrev in *The Chemical Bond. Chemical Bonding Across the Periodic Table* (Eds.: G. Frenking, S. Shaik), Wiley-VCH, Weinheim, **2014**, pp. 421–444.
- [10] I. Fernández, G. Frenking, G. Merino, *Chem. Soc. Rev.* **2015**, *44*, 6452–6463.
- [11] J. M. Mercero, A. I. Boldyrev, G. Merino, J. M. Ugalde, *Chem. Soc. Rev.* **2015**, *44*, 6519–6534.
- [12] S. Blanchard, L. Fensterbank, G. Gontard, E. Lacôte, G. Maestri, M. Malacria, *Angew. Chem. Int. Ed.* **2014**, *53*, 1987–1991; *Angew. Chem.* **2014**, *126*, 2018–2022.
- [13] T. J. Robilotto, J. Bacsá, T. B. Gray, J. P. Sadighi, *Angew. Chem. Int. Ed.* **2012**, *51*, 12077–12080; *Angew. Chem.* **2012**, *124*, 12243–12246.
- [14] T. Kuwabara, J. D. Guo, S. Nagase, M. Saito, *Angew. Chem. Int. Ed.* **2014**, *53*, 434–438; *Angew. Chem.* **2014**, *126*, 444–448.
- [15] F.-X. Pan, L.-J. Li, Y.-J. Wang, J.-C. Guo, H.-J. Zhai, L. Xu, Z.-M. Sun, *J. Am. Chem. Soc.* **2015**, *137*, 10954–10957.
- [16] C. R. Wade, T.-P. Lin, R. C. Nelson, E. A. Mader, J. T. Miller, F. P. Gabbaï, *J. Am. Chem. Soc.* **2011**, *133*, 8948–8955.
- [17] P. Pyykkö, *J. Phys. Chem. A* **2015**, *119*, 2326–2337.
- [18] A. Dragulescu-Andrasi, L. Z. Miller, B. Chen, D. T. McQuade, M. Shatruk, *Angew. Chem. Int. Ed.* **2016**, *55*, 3904–3908; *Angew. Chem.* **2016**, *128*, 3972–3976.
- [19] D. Y. Zubarev, A. I. Boldyrev, *Phys. Chem. Chem. Phys.* **2008**, *10*, 5207–5217.
- [20] A. N. Alexandrova, E. Koyle, A. I. Boldyrev, *J. Mol. Model.* **2006**, *12*, 569–576.
- [21] P. von R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. van Eikema Hommes, *J. Am. Chem. Soc.* **1996**, *118*, 6317–6318.
- [22] M. Giambiagi, M. S. de Giambiagi, C. D. dos Santos Silva, A. P. de Figueiredo, *Phys. Chem. Chem. Phys.* **2000**, *2*, 3381–3392.
- [23] P. Bultinck, R. Ponec, S. Van Damme, *J. Phys. Org. Chem.* **2005**, *18*, 706–718.
- [24] J. Cioslowski, E. Matito, M. Solá, *J. Phys. Chem. A* **2007**, *111*, 6521–6525.
- [25] F. Feixas, E. Matito, M. Duran, J. Poater, M. Solá, *Theor. Chem. Acc.* **2011**, *128*, 419–431.
- [26] F. Feixas, E. Matito, J. Poater, M. Solá, *Chem. Soc. Rev.* **2015**, *44*, 6434–6451.

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