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An All-Metal Aromatic Sandwich Complex $[Sb_3Au_3Sb_3]^{3-}$

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Supporting Information

ABSTRACT: A sandwich complex, as exemplified by ferrocene in the 1950s, usually refers to one metal center bound by two arene ligands. The subject has subsequently been extended to carbon-free aromatic ligands and multiple-metal-atom "monolayered" center, but not to an all-metal species. Here, we describe the synthesis of an unprecedented all-metal aromatic sandwich complex, $[Sb_3Au_3Sb_3]^{3-}$, which was isolated as K([2.2.2]crypt)$^+$ salt and identified by single-crystal X-ray diffraction. Quantum chemical calculations indicate that intramolecular electron transfers for the three metallic layers (Sb → Au donation and Sb ← Au back-donation) markedly redistribute the valence electrons from the *cyclo*-Sb_3 ligands and Au_3 interlayer to the Au−Sb bonds, which hold the complex together via σ bonding. Each *cyclo*-Sb_3 possesses aromaticity with delocalized three-center three-electron (3c-3e) π bonds, which are essentially equivalent to a 3c-4e $\pi\pi^*$ triplet system, following the reversed 4*n* Hückel rule for aromaticity in a triplet state.

The first sandwich complex $(C_5H_5)_2Fe$, termed "ferrocene",[1,2] has sprouted new research disciplines in chemistry and materials science and precipitated tremendous applications in chemical synthesis, catalysis, and material precursors.[3] In 2002, a carbon-free sandwich complex $[(P_5)_2Ti]^{2-}$ was reported, and shortly after that the interlayer was extended from mononuclear metal center to multiple metal atoms.[4−8] These relatively recent findings have expanded the structural concept of sandwich complexes and represent new horizons for materials research. However, an all-metal sandwich complex, in which a metal center or metal sheet is jammed between two aromatic metal rings, has not been isolated, although a large amount of molecules such as $[Al_4TiAl_4]^{2-}$, $[Sb_4FeSb_4]^{2-}$, and $[Sb_5TiSb_5]^{2-}$ has been theoretically proposed, following the discovery of aromatic Al_4^{2-} and $[(P_5)_2Ti]^{2-}$ complexes.[9−16] On the other hand, triggered by the abundance of the triangular Au complexes, sandwich compounds such as $[c\text{-}Au_3(\mu_2\text{-}Cl)_3](C_6H_6)_2$ and $[c\text{-}Au_3(\mu_2\text{-}Cl)_3](B_3N_3H_6)_2$ have also been predicted theoretically.[17] The aforementioned remarkable works have inspired us to explore the possibility to synthesize the all-metal aromatic sandwich complexes. Here we describe the synthesis and characterization of an entirely new cluster anion, $[Sb_3Au_3Sb_3]^{3-}$, in which an Au_3 ring is sandwiched by two *cyclo*-Sb_3.

The $[Sb_3Au_3Sb_3]^{3-}$ complex, crystallized in the form of $[K([2.2.2]crypt)]_3[Sb_3Au_3Sb_3]\cdot(0.5PPh_3)\cdot en$ (**1**; en = ethylenediamine), was isolated by introducing $Au(PPh_3)Ph$ into the ethylenediamine solution of K_5Sb_4 and [2.2.2]crypt. After recrystallization in pyridine (py), **1** could transform to $[K([2.2.2]crypt)]_3[Sb_3Au_3Sb_3]\cdot 3py$ (**2**). The prismatic anion $[Sb_3Au_3Sb_3]^{3-}$ has pseudo-D_{3h} symmetry (Figure 1). To our knowledge, such a ligand-free triangular prismatic structure has never been reported. Furthermore, $[Sb_3Au_3Sb_3]^{3-}$ appears to be the first all-metal aromatic sandwich complex, in which a monolayered metal sheet is jammed between two metallic, aromatic ligands. In the following, only the data of **1** will be presented and discussed.

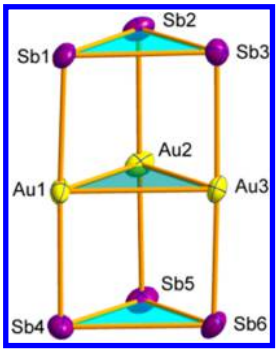

Figure 1. Thermal ellipsoid plot of the molecular cluster anion $[Sb_3Au_3Sb_3]^{3-}$ (drawn at 50% probability). Selected bond distances (angstroms) and angles (degrees): Au1−Au2, 2.9404(6); Au1−Au3, 2.9536(6); Au2−Au3, 2.7179(7); Au1−Sb1, 2.6093(9); Au1−Sb4, 2.5998(10); Au2−Sb2, 2.5992(9); Au2−Sb5, 2.5992(9); Au3−Sb3, 2.5919(9); Au3−Sb6, 2.5939(10); Sb1−Sb2, 2.8615(10); Sb1−Sb3, 2.8708(10); Sb2−Sb3, 2.8489(11); Sb4−Sb5, 2.8648(11); Sb4−Sb6, 2.8619(12); Sb5−Sb6, 2.8824(13); Au2−Au1−Au3, 59.346(15); Au2−Au3−Au1, 60.101(14); Sb2−Sb1−Sb3, 59.60(3); Sb2−Sb3−Sb1, 60.04(3); Sb4−Sb5−Sb6, 59.73(3); Sb4−Sb6−Sb5, 59.83(3).

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In $[Sb_3Au_3Sb_3]^{3-}$ complex, the bond distances of Au−Au (2.918 to 2.954 Å) are confined in a very narrow range (as compared with 2.900 to 3.095 Å in $[Au_3Ge_{18}]^{5-}$),[18a] which are slightly longer than those in typical gold clusters[19] but shorter than those in the Au_3 rings of $[(LAu)_6(N_2)]^{2+}$ (3.244 Å in average; L = $PPh_2{}^iPr$).[18b] Other transition-metal triangles flanked by aromatic arenes were only observed in sandwich complex $[Pd_3(C_7H_7)_2Cl_3]^-$ and related derivatives.[5−7,20−24] However, notable differences set Au_3 apart from Pd_3, because the $[Pd_3(C_7H_7)_2]^{2+}$ core is less stable without the substituents. The Au−Sb distances (2.592 to 2.609 Å) are almost equal with each other, which are markedly shorter than those in complexes (1,8-naphthalene-diyl)$_2$(Ph_2Sb)Au (2.762 Å in average) and [$^nBu_4N$][(1,8-naphthalene-diyl)$_2$(Ph_2SbF)Au] (2.771 Å in average),[25] implying strong Au−Sb interactions in $[Sb_3Au_3Sb_3]^{3-}$. The three Sb−Au−Sb angles are close to 180° (177.87 to 178.15°). As a consequence, Au exhibits linear coordination, and the three metallic layers are virtually coplanar (dihedral angles: 0.08 to 0.39°).

The Sb−Sb distances also span a narrow range within ±0.017 Å (2.849 to 2.882 Å). The Sb_3 units are almost equilateral triangles (59.60 to 60.44°) and bind or accommodate the Au_3 ring favorably via Au−Sb interactions; see below for bonding analysis. The *cyclo*-Sb_3 in $[Sb_3Au_3Sb_3]^{3-}$ also serves as new evidence for the existence of $Sb_3{}^{3-}$ fragment upon dissolving K_5Sb_4 in solvents, which has been put forward for more than 80 years.[26] As predicted by Hagelberg et al.,[27] the *cyclo*-$Sb_3{}^{3-}$ is less-preferred compared with the bent ozone style, which was confirmed by Sevov in experiments.[28] Our results indicate that the *cyclo*-Sb_3 species can be successfully stabilized by the Au_3 ring.

To gain insight into the bonding nature of $[Sb_3Au_3Sb_3]^{3-}$, we have performed quantum chemical calculations at density-functional theory (DFT) level using Gaussian 09 program;[29] see Supporting Information for details. The DFT calculations show that the optimized structure of $[Sb_3Au_3Sb_3]^{3-}$ features an ideal D_{3h} symmetry. The HOMO-LUMO energy gap is calculated to be 3.08 eV, which is surprisingly large in particular for an all-metal complex. $[Sb_3Au_3Sb_3]^{3-}$ possesses nondeltahedral architecture, and thus it no longer follows the conventional Wade's rules.[30] Alternatively, the Sb and Au atoms contribute 18 and 3 valence electrons, respectively, for chemical bonding in the complex (the Sb 5s and Au 5d lone-pairs not included). These 21 electrons in addition to the 3 charges for the overall cluster amount to a total of 24 electrons, which are insufficient for the formation of 15 two-center two-electron (2c-2e) bonds in the triple-layered triangular prism structure (Figure 1). However, the mismatch can be partially offset due to the low bond order for the three Au−Au bonds. The calculated Wiberg bond order[31] of Au−Au is 0.32, which is much smaller than those of Au−Sb (1.09) and Sb−Sb (1.21). Thus, $[Sb_3Au_3Sb_3]^{3-}$ shows relatively weak Au−Au interactions, including aurophilicity as noted by earlier researches.[32−35] By definition, aurophilicity describes the closed-shell interactions between two Au(I) d^{10} centers at the "magic" distance of ∼3 Å, which are of dispersive nature but substantially enhanced in gold due to relativistic effects, comparable in strength to typical hydrogen bonds. In $[Sb_3Au_3Sb_3]^{3-}$, the Au centers are not in the Au(I) state, but the Au 6s electrons appear to participate negligibly in Au−Au bonding; see below. According to the latest recommended covalent radii by Pyykkö,[36,37] typical distances for the Au−Au, Sb−Sb, and Au−Sb single bonds are 2.48, 2.80, and 2.64 Å, respectively. The observed bond distances in $[Sb_3Au_3Sb_3]^{3-}$ are entirely consistent with the calculated Wiberg bond orders.

The potential energy surface of $Sb_3{}^{3-}$ is known to possess two clear minima, representing two $Sb_3{}^{3-}$ species with an equilateral triangle structure and a bent one, respectively.[27] Similar to the isoelectronic ozone molecule, the *cyclo*-$Sb_3{}^{3-}$ is less stable than the bent counterpart (ΔE = 0.5 eV). Nevertheless, the two *cyclo*-Sb_3 in $[Sb_3Au_3Sb_3]^{3-}$ (Figure 1) are equilateral triangles with D_{3h} symmetry, hinting that these Sb_3 ligands are not in $Sb_3{}^{3-}$ charge state. Intramolecular electron transfer occurs between Sb_3 and Au_3 in the present $[Sb_3Au_3Sb_3]^{3-}$ cluster, where the two Sb_3 serve as electron donors and the Au_3 ring as an acceptor. In effect, the two Sb_3 ligands collectively donate three electrons to Au_3, so that three Au 6s based molecular orbitals (MOs) in the latter are occupied (HOMO-15 and HOMO-2/HOMO-2′; Figure 2B).[38]

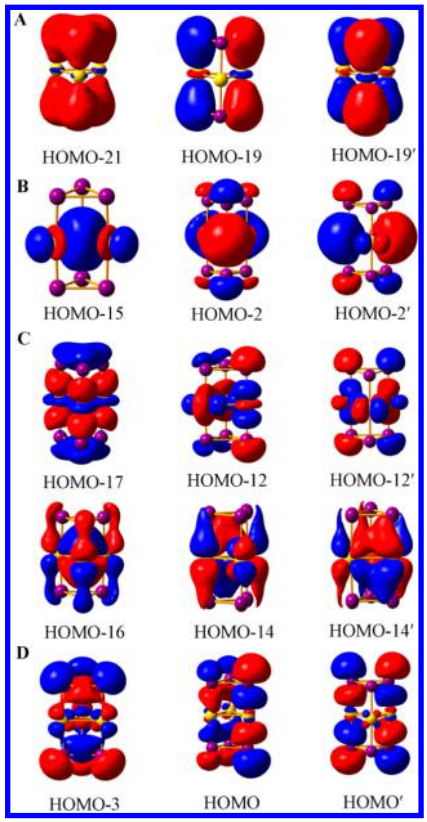

Figure 2. Plots of some key occupied MOs of $[Sb_3Au_3Sb_3]^{3-}$ cluster, generated by GaussView (Sb: purple, Au: yellow).[38] (A) Sb → Au donation: HOMO-21 and HOMO-19/HOMO-19′. (B) Au 6s based MOs: HOMO-15 and HOMO-2/HOMO-2′. The latter two are responsible for Sb → Au donation of 3 electrons. (C) Au → Sb back-donation: HOMO-17, HOMO-12/HOMO-12′, HOMO-16, and HOMO-14/HOMO-14′. (D) Globally delocalized three-center three-electron (3c-3e) bonds in the two *cyclo*-Sb_3: HOMO-3 and HOMO/HOMO′. All these 15 MOs (except HOMO-15) collectively contribute to Au−Sb bonding in $[Sb_3Au_3Sb_3]^{3-}$.

However, complex donation/back-donation processes (Figure 2) drastically redistribute the electrons from three Sb_3 and Au_3 monolayers to six Au−Sb edges, resulting in substantial Au−Sb bonding while reducing the Sb−Sb and Au−Au bond orders. Considering the large electronegativity of Sb, the Au−Sb interaction should be primarily considered as covalent.[39]

To be quantitative, we implement the charge decomposition analysis (CDA; see Table S4).[40] The CDA results show that electron donation and back-donation indeed exist between two *cyclo*-Sb_3 ligands and the Au_3 ring. Specifically, 0.937 e is donated from Sb_3 to Au_3, while 0.241 e is back-donated from Au_3 to Sb_3,

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resulting in weakened Jahn−Teller effect in *cyclo*-Sb_3 with respect to gas-phase Sb_3^{3-} species. According to the CDA, HOMO-21 and HOMO-19/HOMO-19′ contribute partially to electron donation from Sb_3 to Au_3, whereas HOMO-2/HOMO-2′ represent the major donation from Sb_3 to Au_3 (formally by three electrons in total; Figure 2B). On the other hand, HOMO-17, HOMO-16, and relevant MOs contribute to electron back-donation from Au_3 to Sb_3 (Figure 2C). The above 12 MOs distinctly indicate that Au−Sb bonding is covalent in nature, although it is not an equal sharing. It is remarkable that, although not one 2c-2e Au−Sb bond can be identified from the MOs, the donation and back-donation from over 10 MOs (Figure 2) manage to "make" six such bonds, as revealed from the Wiberg bond order and the Au−Sb distances. Donation and back-donation are favorable for covalent bonding, in which the matched electronegativity between the Au and Sb elements should play a pivotal role.

Interestingly, HOMO/HOMO′ and HOMO-3 show delocalized π characters, which are primarily based on two *cyclo*-Sb_3 ligands (Figure 2D). HOMO and HOMO′ are doubly degenerate. Orbital analyses show that HOMO is composed of 90.7% Sb 5p and 9.3% Au 6p, whereas HOMO′ is made up of 95.1% Sb 5p along with 4.9% Au 6p. The components of HOMO-3 include 95.9% Sb 5p and 2.5% Au 6p, with an additional 1.6% Au 5d. In short, the three MOs are primarily derived from Sb 5p atomic orbitals. These π MOs are globally delocalized within two *cyclo*-Sb_3, collectively carrying the three extra charges for the complex. Thus, each *cyclo*-Sb_3 has a formal charge state of $Sb_3^{1.5-}$. This exactly offsets the Sb → Au σ donation (three electrons in total for two Sb_3; Figure 2B), maintaining each *cyclo*-Sb_3 ligand a system with 15 valence electrons (including Sb 5s lone-pairs).[41] The consequence of the bonding pattern is that each Sb_3 effectively has a set of delocalized three-center three-electron (3c-3e) π bonds (Figure 2D). Note that the 3c-3e π bonds are basically equivalent to a typical 3c-4e $\pi\pi^*$ triplet system,[13,42] except that in the former the completely bonding MO and the degenerate, partially bonding MOs are all half-occupied, whereas in a 3c-4e $\pi\pi^*$ triplet system the completely bonding MO is fully occupied. A 3c-4e $\pi\pi^*$ triplet system is known to be aromatic due to the reversed 4*n* Hückel rule for aromaticity in a triplet state,[42] thus the $[Sb_3Au_3Sb_3]^{3-}$ cluster with two 3c-3e π *cyclo*-Sb_3 ligands is π aromatic.[43−45] So far the nucleus-independent chemical shift (NICS) is an efficient probe for aromaticity.[46,47] The calculated $NICS(1)_{zz}$ is −23.13 ppm for each *cyclo*-Sb_3 in $[Sb_3Au_3Sb_3]^{3-}$, consistent with strong π aromaticity for this unique triangular prism cluster. For comparison, $NICS(1)_{zz}$ for benzene is −29.87 ppm at the same level of theory. The above analysis offers new insight for the bonding nature in Au−Sb clusters. We also anticipate that the present all-metal, aromatic sandwich Au−Sb cluster may pave the way for syntheses of entirely new classes of sandwich complexes and find potential technological applications.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b07730.

X-ray crystallographic data (CIF)

Experimental details, selected bond lengths and angles, details on energy-dispersive X-ray and DFT calculations (PDF)

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Notes

The authors declare no competing financial interest.

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(41) As pointed out in the text, the $[Sb_3Au_3Sb_3]^{3-}$ cluster is a system with 24 valence electrons (Au d^{10} and Sb 5s lone-pairs not counted). Of the 15 MOs depicted in Figure 2, the three in Figure 2A are a portion of the six Sb 5s lone-pairs, whereas the six in Figure 2C are six of the Au 5d lone-pairs, at the zeroth order. Thus, only the six MOs in Figures 2B,D belong to the 24 electron counting in $[Sb_3Au_3Sb_3]^{3-}$. The MOs for the remaining 12 valence electrons are responsible for six Sb−Sb σ single bonds, which are not shown in Figure 2.
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(43) While aromaticity is steadily conquering new territories beyond classical aromatic hydrocarbon molecules, some have remained cautious about the concept and only consider it a word.[44] However, aromatic Sb clusters are known in synthetic compounds such as Sb_4^{2-}.[45] Thus, we believe it is appropriate to claim $[Sb_3Au_3Sb_3]^{3-}$ as an aromatic cluster, in particular in the context of the sandwich complexes.
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