### [Sb<sub>4</sub>Au<sub>4</sub>Sb<sub>4</sub>]<sup>2-</sup>: A designer all-metal aromatic sandwich

Wen-Juan Tian', Jin-Chang Guo', Da-Zhi Li', Xue-Rui You, Ying-Jin Wang, Zhong-Ming Sun, and Hua-Jin Zhai'

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### [Sb<sub>4</sub>Au<sub>4</sub>Sb<sub>4</sub>]<sup>2-</sup>: A designer all-metal aromatic sandwich

Wen-Juan Tian,<sup>1,a)</sup> Jin-Chang Guo,<sup>2,a)</sup> Da-Zhi Li,<sup>3,b)</sup> Xue-Rui You,<sup>1</sup> Ying-Jin Wang,<sup>1,2</sup> Zhong-Ming Sun,<sup>4</sup> and Hua-Jin Zhai<sup>1,5,b)</sup>

<sup>1</sup>Nanocluster Laboratory, Institute of Molecular Science, Shanxi University, Taiyuan 030006, China
<sup>2</sup>Department of Chemistry, Xinzhou Teachers University, Xinzhou 034000, China
<sup>3</sup>Department of Chemical Engineering, Binzhou University, Binzhou 256603, China
<sup>4</sup>State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China
<sup>5</sup>State Key Laboratory of Quantum Optics and Quantum Optics Devices, Shanxi University, Taiyuan 030006, China

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We report on the computational design of an all-metal aromatic sandwich,  $[Sb_4Au_4Sb_4]^{2-}$ . The triple-layered, square-prismatic sandwich complex is the global minimum of the system from Coalescence Kick and Minima Hopping structural searches. Following a standard, qualitative chemical bonding analysis via canonical molecular orbitals, the sandwich complex can be formally described as  $[Sb_4]^+[Au_4]^{4-}[Sb_4]^+$ , showing ionic bonding characters with electron transfers in between the  $Sb_4/Au_4/Sb_4$  layers. For an in-depth understanding of the system, one needs to go beyond the above picture. Significant Sb  $\rightarrow$  Au donation and Sb  $\leftarrow$  Au back-donation occur, redistributing electrons from the Sb<sub>4</sub>/Au<sub>4</sub>/Sb<sub>4</sub> layers to the interlayer Sb–Au–Sb edges, which effectively lead to four Sb–Au–Sb three-center two-electron bonds. The complex is a system with 30 valence electrons, excluding the Sb 5s and Au 5d lone-pairs. The two  $[Sb_4]^+$  ligands constitute an unusual three-fold ( $\pi$  and  $\sigma$ ) aromatic system with all 22 electrons being delocalized. An energy gap of ~1.6 eV is predicted for this all-metal sandwich. The complex is a rare example for rational design of cluster compounds and invites forth-coming synthetic efforts. *Published by AIP Publishing*. [http://dx.doi.org/10.1063/1.4959372]

#### I. INTRODUCTION

The past 60 years have witnessed vigorous developments in the sandwich complexes, which were pioneered by ferrocene,  $[(C_5H_5)_2Fe]$ .<sup>1,2</sup> Sandwich complexes have found an array of technical applications in catalysis, chemical synthesis, and as building blocks for new materials. In terms of structural "engineering" of sandwich complexes, the arene ligands were incorporated with group 15 elements, and the transition metal center was extended to actinide in uranocene, U(COT)<sub>2</sub>,<sup>3</sup> and to a monolayered center with multiple metal atoms.<sup>4–6</sup> A carbon-free sandwich [(P<sub>5</sub>)<sub>2</sub>Ti]<sup>2-</sup> complex was also reported.<sup>7</sup> Recently, an all-metal aromatic sandwich  $[Sb_3Au_3Sb_3]^{3-}$  was discovered.<sup>8</sup> Compared to ferrocene, the metal center in  $[Sb_3Au_3Sb_3]^{3-}$  is replaced by an Au<sub>3</sub> monolayer, whereas the arene ligands are switched to two metallic, aromatic Sb<sub>3</sub> rings. The  $[Sb_3Au_3Sb_3]^{3-}$  cluster sets a precedent on the menu of sandwich complexes.

Here we explore the rational design of a new allmetal aromatic sandwich,  $[Sb_4Au_4Sb_4]^{2-}$ , via computational structural searches, electronic structure calculations, and bonding analyses. We show that the all-metal sandwich can be formally described as  $[Sb_4]^+[Au_4]^{4-}[Sb_4]^+$  following standard canonical molecular orbital (CMO) analyses, which is referred to herein as the "zeroth-order ionic picture". However, remarkable Sb  $\rightarrow$  Au donation and Sb  $\leftarrow$  Au back-donation occur, which are typical for covalent bonding. Such processes redistribute electrons from the Sb<sub>4</sub>/Au<sub>4</sub>/Sb<sub>4</sub> layers to the interlayer edges, effectively resulting in four Sb–Au–Sb three-center two-electron (3c-2e) bonds, which underlie the stability of the sandwich. The two [Sb<sub>4</sub>]<sup>+</sup> ligands are shown to be  $\pi$  and  $\sigma$  aromatic, whose all 22 valence electrons are completely delocalized in three-fold nature, representing a highly unusual chemical bonding system. In terms of the electronic property, this all-metal sandwich is predicted to possess a moderate energy gap of ~1.6 eV, suggesting that it may behave like a semiconductor.

Designing nanoclusters with desirable properties and assembling them into nanomaterials have been a longsought goal in nanoscience, which is routinely described as the so-called "bottom-up" approach. All-metal sandwich clusters with a single metal center, such as  $[Al_4TiAl_4]^{2-}$  and  $[Sb_5TiSb_5]^{2-}$ , were designed previously.<sup>9–11</sup> However, those are considered to be model systems because the two metallic ligands are susceptible to coalescence. The  $[Sb_4Au_4Sb_4]^{2-}$ cluster has a dimension of about 0.5 nm. We believe this all-metal aromatic sandwich is a rare example for rational design of novel clusters, which may be an intriguing target for bulk syntheses.

### **II. METHODS SECTION**

The Coalescence Kick  $(CK)^{12,13}$  and Minima Hopping  $(MH)^{14-16}$  algorithms were used for the global-minimum structural searches. A total of about 1300 stationary points

<sup>&</sup>lt;sup>a)</sup>W.-J. Tian and J.-C. Guo contributed equally to this work.

<sup>&</sup>lt;sup>b)</sup>Authors to whom correspondence should be addressed. Electronic addresses: hj.zhai@sxu.edu.cn and ldz005@126.com.

for the  $[Sb_8Au_4]^{2-}$  dianion system were probed in the CK and MH searches. Candidate low-lying structures were subsequently fully optimized at the PBE0/def2-tzvp level.<sup>17,18</sup> Harmonic vibrational frequencies were calculated at the same level to compute the zero-point energies and to verify that the reported structures are true minima on the potential energy surface. The top structures within 0.6 eV were also optimized at the PBE0/aug-cc-pvtz-pp level<sup>17,19</sup> to evaluate their relative energies. The energetics for top two structures were further calibrated using the single-point calculations at the coupled-cluster with single and double and perturbative triple excitations (CCSD(T)) level.

The CMO and adaptive natural density partitioning (AdNDP)<sup>20</sup> analyses were performed to understand the chemical bonding in the complex. Natural bond orbital (NBO) analysis was carried out to get the natural atomic charges and the Wiberg bond indices (WBIs).<sup>21</sup> The AdNDP analyses were performed using the AdNDP program, and all other calculations and analyses were performed using the Gaussian 09 package.<sup>22</sup>

#### **III. RESULTS AND DISCUSSION**

### A. Global-minimum $[Sb_4Au_4Sb_4]^{2-}$ as a square-prismatic, all-metal sandwich

Global-minimum searches for the  $[Sb_8Au_4]^{2-}$  dianion system were performed, independently, using the CK and MH algorithms, aided with manual structural constructions. Candidate low-lying structures were fully optimized at PBE0/def2-tzvp and PBE0/aug-cc-pvtz-pp levels, with complementary calculations at B3LYP/aug-cc-pvtz-pp and single-point CCSD(T). As shown in Figs. 1 and 2, the global minimum of  $[Sb_8Au_4]^{2-}$  is  $D_{4h}$  ( ${}^{1}A_{1g}$ ), being reasonably well separated from alternative structures by at least 0.2 eV. Note that the energetics at single-point CCSD(T) for top two isomeric structures is highly consistent with that at PBE0, which serves as a benchmark for the PBE0 method. In the following, we shall mainly focus on the data at PBE0. The minimum vibrational frequency of  $[Sb_4Au_4Sb_4]^{2-} D_{4h}$  ( ${}^{1}A_{1g}$ ) is anticipated to be small due to the heavy Au and Sb



FIG. 1. Optimized  $D_{4h}$  (<sup>1</sup>A<sub>1g</sub>) global-minimum structure of [Sb<sub>4</sub>Au<sub>4</sub>Sb<sub>4</sub>]<sup>2-</sup> at the PBE0/aug-cc-pvtz-pp level. The Au atom is in yellow and Sb in purple. The bond distances, bond angles, and electronic property are collected in Table I.

GHTSLINKA)

elements in the system. Nonetheless, the calculated numbers (degenerate mode) amount to +8.3/+8.3, +26.2/+26.2, +9.6/+9.6, and +25.9/+25.9 cm<sup>-1</sup> at the PBE0/def2-tzvp, B3LYP/def2-tzvp, PBE0/aug-cc-pvtz-pp, and B3LYP/aug-cc-pvtz-pp levels, respectively. Thus, with the PBE0 and B3LYP functionals, as well as smaller def2-tzvp and larger aug-cc-pvtz-pp basis sets, the calculated values for minimum frequency are consistently positive. In particular, PBE0 and B3LYP are widely considered to be complementary methods and thus when they predict the same minimum as for [Sb<sub>4</sub>Au<sub>4</sub>Sb<sub>4</sub>]<sup>2-</sup>  $D_{4h}$  (<sup>1</sup>A<sub>1g</sub>), it is a true minimum on the potential energy surface.

All alternative low-lying  $Sb_8Au_4^{2-}$  structures possess lower  $C_1$  symmetry (Fig. 2), in contrast to the  $D_{4h}$  global minimum. We would like to comment that alternative charge states may be possible for the  $[Sb_4Au_4Sb_4]$  all-metal sandwich. The  $[Sb_4Au_4Sb_4]^{2-}$  charge state is simply our favorable choice, which turns out to have an ideal electron configuration. The dianion nature of  $[Sb_4Au_4Sb_4]^{2-}$  should not be a problem for synthesis as bulk compounds, in light of the fact that  $[Sb_3Au_3Sb_3]^{3-}$  trianion was reported as the first all-metal sandwich complex.<sup>8</sup> The  $[Sb_4Au_4Sb_4]^-$  monoanion charge state may be stable as a gas-phase species, but it is subject to structural distortion owing to the open-shell nature.

The  $D_{4h}$  (<sup>1</sup>A<sub>1g</sub>) global minimum of [Sb<sub>4</sub>Au<sub>4</sub>Sb<sub>4</sub>]<sup>2-</sup> (Fig. 1) adopts a highly symmetric, triple-layered, square-prismatic structure, which is composed of a square-planar Au<sub>4</sub> interlayer sandwiched in between two square-planar Sb<sub>4</sub> clusters. The bond angle  $\angle$ SbAuSb is 176.95° (Table I), indicating that the four Sb-Au-Sb edges are almost linear. The Sb-Sb, Au–Au, and Sb–Au distances are 2.849, 2.948, and 2.636 Å, respectively, which are to be compared with the recommended upper bound for their single bonds (2.80, 2.48, and 2.64 Å).<sup>23</sup> The distances suggest that the Sb-Sb and Sb-Au bonds are comparable to single bonds and the Au-Au interaction is weak, in line with the calculated Wiberg bond indices (Sb-Sb: 0.99; Sb-Au: 0.66; Au-Au: 0.25; see Table II). The Sb-Sb distance in [Sb<sub>4</sub>Au<sub>4</sub>Sb<sub>4</sub>]<sup>2-</sup> is comparable to that in  $[Sb_3Au_3Sb_3]^{3-}$   $(2.85\text{--}2.88\ \text{\AA})^8$  but markedly longer than that in the  $[Sb_4]^{2-}$  compound (2.75 Å),<sup>24</sup> hinting that the square Sb<sub>4</sub> rings in  $[Sb_4Au_4Sb_4]^{2-}$  are not in the Sb<sub>4</sub><sup>2-</sup> charge state.

### B. Chemical bonding via molecular orbital analysis: Three-fold aromaticity

To elucidate the bonding nature in  $[Sb_4Au_4Sb_4]^{2-}$ , it is essential to perform an analysis of the CMOs. The Sb and Au atoms have electronic configurations of  $5s^25p^3$  and  $5d^{10}6s^1$ , respectively. In  $[Sb_4Au_4Sb_4]^{2-}$  complex, the Sb  $5s^2$  and Au  $5d^{10}$  electrons are approximately considered to be lone-pairs and can be identified from their corresponding CMOs in Figs. 3 and 4, as well as in Fig. S1 of the supplementary material.<sup>25</sup> For example, the set of CMOs in Fig. 3 correspond to 8 Sb 5s lone-pairs, one on every Sb center.<sup>26</sup> Similarly, all CMOs depicted in Fig. S1 are readily approximated to 20 Au 5d lone-pairs, 5 for each Au center ( $d_{xy}$ ,  $d_{yz}$ ,  $d_{xz}$ ,  $d_{x^2-y^2}$ , and  $d_{z^2}$ ). These lone-pairs (8 for Sb 5s and 20 for Au d<sup>10</sup>) are born out from the AdNDP analysis; see Figs. S2(a) and S2(b).<sup>25</sup> Note that the lone-pairs are only a simplified view.



FIG. 2. Low-lying structures of  $[Sb_8Au_4]^{2-}$  cluster at the PBE0/def2-tzvp level. Only those isomers of relative energies within 1.0 eV are shown. Also shown are the relative energies at PBE0/aug-cc-pvtz-pp (in parentheses) for top low-lying isomers and those at the single-point CCSD(T)//PBE0/def2-tzvp (in curly brackets) and CCSD(T)//B3LYP/def2-tzvp (in square brackets) for first two isomers. The PBE0/aug-cc-pvtz-pp data are considered to be reliable and complete, and the single-point CCSD(T) data serve as a benchmark for the PEE0 method.

As further analyses will show, there are no "ideal" lone-pairs in  $[Sb_4Au_4Sb_4]^{2-}$ .

Apart from Sb  $5s^2$  and Au  $5d^{10}$  lone-pairs, the  $[Sb_4Au_4Sb_4]^{2-}$  complex is a system with 30 valence electrons  $(5p^3 \text{ for Sb}, 6s^1 \text{ for Au}, \text{ plus two extra electrons})$ , which are insufficient for the 8 Sb–Sb, 4 Au–Au, and 8 Sb–Au links. The electron counting reveals an unusual bonding system: 30 electrons versus 20 Sb–Sb/Au–Au/Sb–Au links. The 30 electrons occupy eleven Sb 5p based CMOs (Fig. 5) and four Au 6s based ones (Fig. 6(a)). The latter CMOs indicate

that eight electrons participate in the Au 6s based bonding, including the highest occupied molecular orbital (HOMO) occupied by two extra electrons in the dianion. The two Sb<sub>4</sub> rings should provide two electrons in order to fulfill these four CMOs. Thus, in a formal, ionic picture based on the CMO analyses  $[Sb_4Au_4Sb_4]^{2-}$  should be formulated as  $[Sb_4]^+[Au_4]^{4-}[Sb_4]^+$ , although the essence of bonding in the system is far more covalent.

The eleven Sb 5p derived CMOs (Fig. 5) constitute an interesting bonding system. Consistent with the above

TABLE I. Bond distances (in Å), bond angles (in degrees), and HOMO-LUMO energy gap (in eV) for  $[Sb_4Au_4Sb_4]^{2-}$  at the PBE0/aug-cc-pvtz-pp and B3LYP/aug-cc-pvtz-pp levels.

Method	r <sub>Sb-Sb</sub>	r <sub>Au-Au</sub>	r <sub>Sb-Au</sub>	∠SbAuSb	ΔE <sub>HOMO-LUMO</sub>
PBE0	2.849	2.948	2.636	176.95	1.63
B3LYP	2.887	3.097	2.676	173.66	1.56

zeroth-order ionic picture, the two [Sb<sub>4</sub>] units are in formal oxidation state of  $[Sb_4]^+$  and possess 22 electrons in total. The  $p_x$ ,  $p_y$ , and  $p_z$  atomic orbitals (AOs) of the Sb centers can, in principle, form 8 radial  $p_{\sigma-r}$ , 8 tangential  $p_{\sigma-t}$ , and 8  $p_{\pi}$  CMOs<sup>27,28</sup> for [Sb<sub>4</sub>Au<sub>4</sub>Sb<sub>4</sub>]<sup>2-</sup>; that is, 24 CMOs in total. A set of these 8 CMOs are divided into two subsets, each being presumably in the combination of bonding, degenerate partial bonding/antibonding, and antibonding (that is, in the spirit of Sb 5s based CMOs; Figs. 3 and 4). However, only 22 electrons are available to occupy these CMOs. In other words, only 11 out of the above 24 Sb 5p-based CMOs are to be occupied in the all-metal sandwich: 3  $p_{\sigma-r}$ , 2  $p_{\sigma-t}$ , and 6  $p_{\pi}$  (Fig. 5). A simple counting of the CMOs for each subset indicates that none of the  $p_{\sigma-r}$ ,  $p_{\sigma-t}$ , and  $p_{\pi}$  frameworks can be localized as 2c-2e bonds or lone-pairs, because a completely localized subsystem for the Sb-Sb links requires a subset of eight CMOs, not just 3, 2, or 6. Thus, the all-metal sandwich has to feature three-fold electron delocalization.

To be more specific, the tangential  $p_{\sigma-t}$  framework of the sandwich consists of two CMOs (Fig. 5(b)), being completely bonding within the Sb<sub>4</sub> squares but in a constructive/destructive combination between the two squares. These are readily transformed to two 4c-2e  $p_{\sigma-t}$  bonds, each of which is delocalized and completely bonding within a Sb<sub>4</sub> square and cannot be further localized, rendering  $\sigma_t$  aromaticity for the Sb<sub>4</sub> rings according to the (4*n* + 2) Hückel rule.

On the other hand, the three  $p_{\sigma-r}$  CMOs (Fig. 5(a)) are the constructive combination of radial  $\sigma$  orbitals between the two Sb<sub>4</sub> rings. As an example, Fig. 7 illustrates how these three  $p_{\sigma-r}$  CMOs (middle panel) are built from the  $p_{\sigma-r}$  orbitals of two  $D_{4h}$  Sb<sub>4</sub> ligands (left and right panels). Each ligand only needs to contribute a single electron in order to form a CMO of the sandwich. The  $p_{\sigma-r}$  framework has six electrons in total (with eight Sb–Sb links), which are not sufficient for transformation to 4c-2e bonds, 2c-2e bonds, or lone-pairs. Thus, the  $p_{\sigma-r}$  framework is completely delocalized. However, the  $p_{\sigma-r}$  CMOs (an 8c-6e system) may be equivalently viewed as two 4c-3e systems combined (Fig. 7), in which one bonding and two degenerate, partially bonding/antibonding CMOs within a Sb<sub>4</sub> square are all half-occupied. This situation is closely relevant to a typical 4-electron  $\pi\pi^*$  triplet species,<sup>29,30</sup>

TABLE II. Wiberg bond indices (WBIs) and natural charges (in |e|) for  $[Sb_4Au_4Sb_4]^{2-}$  at the PBE0/aug-cc-pvtz-pp and B3LYP/aug-cc-pvtz-pp levels.

Method	WBI <sub>Sb-Sb</sub>	WBI <sub>Sb-Au</sub>	WBI <sub>Au-Au</sub>	$q_{Sb}$	$q_{Au}$
PBE0	0.99	0.66	0.25	-0.097	-0.305
B3LYP	1.00	0.64	0.21	-0.109	-0.282



FIG. 3. Pictures of the occupied canonical molecular orbitals (CMOs) responsible for the Sb 5s lone-pairs in  $[Sb_4Au_4Sb_4]^{2-}$  cluster. There are 8 such CMOs in total.

which is known to be aromatic following the reversed 4n Hückel rule. Alternatively, the  $p_{\sigma-r}$  4c-3e Sb<sub>4</sub> system can be compared to a model, square-planar 4c-6e system. The latter has 3 fully occupied CMOs and is aromatic, and thus, the former with three half-occupied orbitals should be half as aromatic.

For the  $p_{\pi}$  framework in  $[Sb_4Au_4Sb_4]^{2-}$ , the 6 CMOs (Fig. 5(c)) are all destructive combinations between two Sb<sub>4</sub> squares, which can be divided into two sextets: HOMO–5/HOMO–1/HOMO–1' versus HOMO–7/HOMO–2/ HOMO–2'. As an approximate 8c-12e delocalized  $\pi$  system, the  $p_{\pi}$  framework is equivalent to two 4c-6e  $\pi$  subsystems within the two Sb<sub>4</sub> ligands, which render  $\pi$  aromaticity for the all-metal sandwich, following the reversed 4*n* Hückel rule.<sup>29,30</sup>

Bowen and coworkers recently reported  $\sigma$  aromaticity, as well as double  $\sigma$  and  $\pi$  aromaticity, in metal clusters.<sup>31,32</sup> Based on the above analyses, the radial  $p_{\sigma-r}$ , tangential  $p_{\sigma-t}$ , and perpendicular  $p_{\pi}$  frameworks in  $[Sb_4Au_4Sb_4]^{2-}$  are all delocalized systems, collectively leading to three-fold ( $\sigma_r$ ,  $\sigma_t$ , and  $\pi$ ) aromaticity.<sup>27,28</sup> Note that all these 11 delocalized CMOs are recovered from AdNDP (Fig. S2).<sup>25</sup> Square-planar

HOMO-5 (b<sub>1g</sub>) HOMO-6 (e<sub>u</sub>) HOMO-6' (e<sub>u</sub>) HOMO-7 (a<sub>1g</sub>)

FIG. 4. Pictures of the selected canonical molecular orbitals (CMOs) in a model  $D_{4h}$  Sb<sub>4</sub> cluster. The CMOs are based on Sb 5s atomic orbitals (AOs), which can in turn be transformed to four Sb 5s<sup>2</sup> lone-pairs.



FIG. 5. The delocalized canonical molecular orbitals (CMOs) for bonding within the two Sb<sub>4</sub> ligands in  $[Sb_4Au_4Sb_4]^{2-}$ . These are primarily eight-center two-electron (8c-2e) in nature, with secondary contributions from the Au<sub>4</sub> interlayer.

 $[Sb_4]^{2-}$  dianion cluster is known as a synthetic compound since the 1980s,<sup>24</sup> albeit its aromaticity and its  $\pi$  sextet were not elucidated until 2002.<sup>33</sup> A sandwich complex such as  $[Sb_4Au_4Sb_4]^{2-}$  can offer a rich variety of aromaticity and alter the electron counting rules.<sup>30</sup> This is possible mainly because in a sandwich complex, the two ligands can couple in different ways, so that for each CMO associated with aromaticity one ligand only needs to provide one electron (rather than two; see Fig. 7 for an example) without the sacrifice of aromaticity for the sandwich. Indeed, the 11 electrons in an  $[Sb_4]^+$  ligand manage to participate in three-fold ( $\pi$ ,  $\sigma$  radial, and  $\sigma$  tangential) aromaticity, contributing barely 6, 3, and 2 electrons, respectively (Fig. 5).

It is a bit beyond imagination that for a system of two Sb<sub>4</sub> squares with 22 electrons, not a single 2c-2e bond can be identified. An intuitive guess would suggest at least eight Sb–Sb 2c-2e bonds, which turns out to be wrong! For comparison, the  $[Sb_3Au_3Sb_3]^{3-}$  complex<sup>8</sup> only has 6 delocalized electrons. We should summarize that the three-fold aromaticity of the all-metal sandwich is established here on the bases of multiple criteria: (i) structure ( $D_{4h}$  symmetry), (ii) electron counting according to the reversed 4n Hückel rule,<sup>30</sup> (iii) CMO analysis, and (iv) AdNDP. The data from the criteria are concerted for the present system. Of these, the CMOs are the most fundamental criterion, which has been extensively analyzed and discussed throughout the text. AdNDP may be viewed as an alternative and independent version of the CMO analysis.

# C. Bound mechanism underlies the all-metal sandwich: Charge redistribution from the Sb<sub>4</sub>/Au<sub>4</sub>/Sb<sub>4</sub> layers to the interlayer Sb–Au–Sb edges

The above zeroth-order bonding picture indicates that  $[Sb_4Au_4Sb_4]^{2-}$  is intrinsically a three-layered sandwich, whose 30 electrons consist of 4 Au 6s based CMOs for the middle Au<sub>4</sub> sheet and 11 Sb 5p based CMOs for the upper and lower Sb<sub>4</sub> rings. Two questions remain open: Why is there only

minimal Au–Au bonding despite four Au 6s based CMOs? How are the three Sb<sub>4</sub>/Au<sub>4</sub>/Sb<sub>4</sub> layers bounded together for a sandwich? The CMO, NBO, and AdNDP analyses help address these critical issues.

The calculated Wiberg bond order for Au–Au is ~0.2 (Table II). This is in contrast to the four Au 6s based CMOs (Fig. 6(a)), which point to a formal bond order of 1.0. As stated above, in an zeroth-order ionic picture, the complex can be formulated as  $[Sb_4]^+[Au_4]^{4-}[Sb_4]^+$ , where the Sb and Au centers are in charge states of +0.25 and -1, respectively. However, the calculated natural charges are -0.1 for Sb and -0.3 for Au (Table II). We believe the key to reconcile the discrepancies lies in the fact that the Sb–Au interaction is rather covalent due to their compatible electronegativity: 2.54 for Au versus 2.05 for Sb at the Pauling scale. The bonding covalency is manifested vividly via Sb  $\rightarrow$  Au donation and Sb  $\leftarrow$  Au back-donation.

As illustrated in Fig. 6, some 24 CMOs participate in electron redistribution from the Sb<sub>4</sub>/Au<sub>4</sub>/Sb<sub>4</sub> layers to the interlayer Sb-Au edges, which manages to build 8 Sb-Au "bonds" with reasonable strength (Wiberg order: 0.66), despite the fact that not a single Sb-Au bonding CMO can be identified in the system. Note that 14 of these CMOs (Figs. 6(b) and 6(d) belong to portion of the Sb 5s or Au 5d lonepairs, suggesting that there are probably no pure lone-pairs in the system. Of the 24 CMOs, HOMO-4/HOMO-4' are responsible for the Sb  $\rightarrow$  Au donation of formally two electrons. Nonetheless, these CMOs possess the components of 70% Au s/p/d versus 28% Sb s/p, suggesting that only half of an electron is actually transferred for each CMO. The two extra electrons in the dianion are hosted by the HOMO, which has 52% Au s/d versus 32% Sb p, and thus, the two charges are roughly split: one for Au<sub>4</sub> and half for each Sb<sub>4</sub> ligand. For the Sb  $\leftarrow$  Au back-donation, the key CMOs are HOMO-15 (60% Au d versus 40% Sb s) and HOMO-25 (48% Au s/d versus 48% Sb p), which represent the transfer of roughly two electrons. Other CMOs in Fig. 6 all contain a minor component from 4% up to 24%. These



FIG. 6. Plots of selected key CMOs of  $[Sb_4Au_4Sb_4]^{2-}$  cluster. (a) Au 6s based CMOs, among which HOMO-4/HOMO-4' involve major Sb  $\rightarrow$  Au donation for two electrons formally and HOMO accepts the two extra charges. (b) Sb  $\rightarrow$  Au donation from portion of the CMOs responsible for Sb 5s lone-pairs. (c) Sb  $\rightarrow$  Au donation from portion of the CMOs responsible for delocalized bonding within the Sb<sub>4</sub> ligands. (d) Sb  $\leftarrow$  Au back-donation from portion of the CMOs primarily responsible for Au 5d lone-pairs.

complicated donation and back-donation processes make the Sb–Au interactions highly covalent, collectively "building" four 3c-2e Sb–Au–Sb bonds (Fig. 8) and leading to the calculated NBO charges of -0.3 for Au and -0.1 for Sb (Table II).

Due to the reduced bond order, the Au–Au bonding in  $[Sb_4Au_4Sb_4]^{2-}$  is primarily attributed to aurophilicity,<sup>34,35</sup> which describes the closed-shell interaction between two Au(I) d<sup>10</sup> centers at a magic distance of ~3.0 Å. Aurophilicity is sort of unusual, being dispersive in nature akin to van der Waals interactions, but it is substantially enhanced (7–12 kcal/mol; comparable in strength to hydrogen bonds) due to relativistic effects for Au.<sup>36</sup> As in the case of  $[Sb_4Au_4Sb_4]^{2-}$ , the Au centers are not in the oxidation state of Au(I). However, the large Au–Au distances indicate that aurophilicity dominates Au–Au bonding in the all-metal sandwich.

## D. On the four 3c-2e Sb–Au–Sb $\sigma$ bonds in $[Sb_4Au_4Sb_4]^{2-}$

The net Sb–Au interactions in  $[Sb_4Au_4Sb_4]^{2-}$ , due to the complicated electron donation and back-donation processes from over 20 CMOs (Fig. 6), are technically quantified via the AdNDP analysis. As shown in Fig. 8, a total of four 3c-2e Sb–Au–Sb edge bonds are revealed from AdNDP, with perfect occupation numbers (ONs) of 1.99. These 3c-2e Sb–Au–Sb  $\sigma$  bonds do not correspond to any specific CMOs in the system, rather they are the contributions from over 20 CMOs, which is a remarkable collective effect. The collective 3c-2e bonds roughly interpret the calculated Wiberg bond order for Sb–Au (0.66 at PBE0; Table II), which is the key mechanism that bounds three Sb<sub>4</sub>/Au<sub>4</sub>/Sb<sub>4</sub> layers for a unique all-metal sandwich.



FIG. 7. A schematic diagram showing how the orbitals from two  $D_{4h}$  Sb<sub>4</sub> ligands combine to form the CMOs of  $D_{4h}$  [Sb<sub>4</sub>Au<sub>4</sub>Sb<sub>4</sub>]<sup>2-</sup> sandwich, using the radial  $p_{\sigma-r}$  framework (Fig. 5(a)) as an example.



FIG. 8. AdNDP bonding pattern for four three-center two-electron (3c-2e) Sb–Au–Sb  $\sigma$  bonds in [Sb<sub>4</sub>Au<sub>4</sub>Sb<sub>4</sub>]<sup>2–</sup>. None of these bonds can be identified from any specific CMO, rather they reflect the collective effects of the Sb  $\rightarrow$  Au donation and Sb  $\leftarrow$  Au back-donation from over 20 CMOs (Fig. 6). The occupation numbers (ONs) are indicated.

#### **IV. CONCLUSIONS**

In conclusion, we have designed an all-metal aromatic sandwich,  $[Sb_4Au_4Sb_4]^{2-}$ . The triple-layered, squareprismatic complex is the global minimum of the system via Coalescence Kick and Minima Hopping structural searches. In a formal, ionic picture based on the analyses of canonical molecular orbitals, the sandwich complex can be formulated as  $[Sb_4]^+[Au_4]^{4-}[Sb_4]^+$ . The system has 30 valence electrons, which are insufficient for the 8 Sb–Sb, 4 Au–Au, and 8 Au–Sb links. Bonding analyses show that the two  $[Sb_4]^+$ ligands possess three-fold ( $\pi$ ,  $\sigma$  radial, and  $\sigma$  tangential) aromaticity, whose all 22 electrons are delocalized. The interlayer Sb–Au interactions appear to be covalent via complicated donation and back-donation processes, which are collectively quantified as four Sb–Au–Sb three-center two-electron bonds. Furthermore, a HOMO–LUMO gap of  $\sim$ 1.6 eV is predicted for the all-metal sandwich. This designer all-metal aromatic sandwich invites forth-coming synthetic efforts.

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- <sup>25</sup>See supplementary material at http://dx.doi.org/10.1063/1.4959372 for the optimized Cartesian coordinates for  $[Sb_4Au_4Sb_4]^{2-}$  at PBE0/aug-cc-pvtz-pp and B3LYP/aug-cc-pvtz-pp levels; pictures of selected occupied canonical molecular orbitals (CMOs) in a model  $D_{4h}$  Sb<sub>4</sub> cluster and those for the Au d<sup>10</sup> lone-pairs in  $[Sb_4Au_4Sb_4]^{2-}$ ; and the AdNDP bonding pattern for  $[Sb_4Au_4Sb_4]^{2-}$ .
- <sup>26</sup>For Sb 5s<sup>2</sup>, the 8 atomic orbitals (AOs) combine to form 8 CMOs (Fig. 3). All these CMOs are practically eight-center two-electron (8c-2e) in nature, being based on the two Sb<sub>4</sub> squares. There are four pairs of constructive/destructive combinations for them (Fig. 3; left panel versus

right panel). Each pair can be recombined to form two 4c-2e orbitals on the Sb<sub>4</sub> rings. Consequently, the Sb<sub>4</sub> ring has four Sb 5s based orbitals in a classical combination of completely bonding, degenerate partial bonding/antibonding, and completely antibonding (Fig. 4), which in turn can be transformed to four Sb 5s lone-pairs.

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