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Theoretical Probing of Deltahedral *closo*-AuroBoranes $B_xAu_x^{2-}$ ($x = 5$–12)

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Using density functional theory calculations, here we show that a series of $B_xAu_x^{2-}$ ($x = 5$–12) dianions possesses structure and bonding similar to the famous deltahedral *closo*-borane cages, $B_xH_x^{2-}$. Effective atomic charges on Au in $B_xAu_x^{2-}$ are very similar to those on H in $B_xH_x^{2-}$, indicating that Au in the *closo*-auroboranes is indeed analogous to H in the *closo*-boranes. The present theoretical predictions of $B_xAu_x^{2-}$ suggest that the *closo*-auroborane species are viable new chemical building blocks that may be synthesized in bulk. The Au atoms in the *closo*-auroboranes represent highly atomically dispersed Au and may potentially exhibit novel catalytic and chemical properties.

Since the discovery of boron hydrides (boranes) by Stock and Massanez in 1912,[1] these compounds have played a major role in advancing chemical bonding theory beyond the classical idea of two-center, two-electron (2c-2e) bonds. Longuet-Higgins, Lipscomb, and co-workers[2,3] first put forward the concept of three-center, two-electron bonding to explain the structures of all known boron hydrides, in which the bridging B−H−B bond appeared to be the key structural unit.[4] This represents a milestone in establishing the validity of the molecular orbital theory.

In particular, the *closo*-boranes ($B_xH_x^{2-}$) have aesthetically pleasing symmetries because their structures are based on deltahedral B cages. Of particular interest is the icosahedral $B_{12}H_{12}^{2-}$ dianion, which was first synthesized by Hawthorne and Pitochelli in 1960,[5] shortly after its theoretical prediction by Longuet-Higgins and Roberts in 1955.[6] In recent years, Hawthorne and co-workers have synthesized and determined the structures of many compounds containing substituted *closo*-$B_{12}R_{12}^{2-}$ (R = Me, OH, OCH_2Ph, OCOPh) dianions,[7] thus significantly enriching the chemistry of *closo*-boranes and their potential applications. Here we predict a new class of *closo*-auroboranes $B_xAu_x^{2-}$ and present theoretical evidence showing that $B_xAu_x^{2-}$ can be viable new gold-rich compounds. While, to the best of our knowledge, there are no published experimental data on $B_xAu_x^{2-}$ *closo*-auroboranes, there are many known Au−carborane complexes.[8,9] Mitchel and Stone,[8a] Reid and Welch,[8b] and Baukova et al.[8c] reported examples of *closo*-carboranes with Au bonded to C by 2c-2e σ bonds. Stone and co-workers reported the synthesis and characterization of a series of *nido*-carboranes interacting with Au via cluster bonding.[8d−h] Hawthorne and co-workers synthesized and characterized aurocarboranes with C−Au 2c-2e bonds with and without Au−Au interactions.[8i] Wesemann and co-workers reported

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(1) (a) Stock, A.; Massanez, C. *Chem. Ber*. **1912**, *45*, 3539. (b) Stock, A. *Hydrides of Boron and Silicon*; Cornell University Press: Ithaca, NY, 1933.

(2) Bell, R. P.; Longuet-Higgins, H. C. *Nature* **1945**, *155*, 328.

(3) Eberhardt, W. H.; Crawford, B.; Lipscomb, W. N. *J. Chem. Phys*. **1954**, *22*, 989.

(4) Lipscomb, W. N. *Boron Hydride Chemistry*; Academic Press: New York, 1975.

(5) Hawthorne, M. F.; Pitochelli, A. R. *J. Am. Chem. Soc.* **1960**, *82*, 3228.

(6) Longuet-Higgins, H. C.; Roberts, M. de, V. *Proc. R. Soc. London, Ser. A* **1955**, *230*, 110.

(7) (a) Peymann, T.; Knobler, C. B.; Khan, S. I.; Hawthorne, M. F. *Inorg. Chem*. **2001**, *40*, 1291. (b) Peymann, T.; Herzog, A.; Knobler, C. B.; Hawthorne, M. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 1061. (c) Bayer, M. J.; Hawthorne, M. F. *Inorg. Chem*. **2004**, *43*, 2018. (d) Farha, O. K.; Julius, R. L.; Lee, M. W.; Huertas, R. E.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc*. **2005**, *127*, 18243.

(8) (a) Mitchell, C. M.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1970**, 1263. (b) Reid, B. D.; Welch, A. J. *J. Organomet. Chem*. **1992**, *438*, 371. (c) Baukova, T. V.; Kuz'mina, L. G.; Dvortsova, N. V.; Porai-Koshits, M. A.; Kravtsov, D. N.; Perevalova, E. G. *Metalloorg. Khim.* **1989**, *2*, 1098. (d) Howard, J. A. K.; Jeffery, J. C.; Jelliss, P. A.; Sommerfeld, T.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun*. **1991**, 1664. (e) Jeffery, J. C.; Jelliss, P. A.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans*. **1993**, 1073. (f) Jeffery, J. C.; Jelliss, P. A.; Stone, F. G. A. *Inorg. Chem*. **1993**, *32*, 3943. (g) Jeffery, J. C.; Jelliss, P. A.; Stone, F. G. A. *Organometallics* **1994**, *13*, 2651. (h) Jeffery, J. C.; Jelliss, P. A.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans*. **1994**, 25. (i) Harwell, D. E.; Mortimer, M. D.; Knobler, C. B.; Anet, F. A. L.; Hawthorne, M. F. *J. Am. Chem. Soc*. **1996**, *118*, 2679.

(9) (a) Hagen, S.; Pantenburg, I.; Weigend, F.; Wickleder, C.; Wesemann, L. *Angew. Chem., Int. Ed.* **2003**, *42*, 1501. (b) Marx, T.; Mosel, B.; Pantenburg, I.; Hagen, S.; Schulze, H.; Wesemann, L. *Chem.−Eur. J.* **2003**, *9*, 4472. (c) Hagen, S.; Wesemann, L.; Pantenburg, I. *Chem. Commun*. **2005**, 1013.

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the synthesis and characterization of gold−tin−*closo*-borate compounds with Sn−Au bonds.[9] Au−B compounds were summarized in a recent review.[10]

There are also a few compounds not related to boranes or carboranes, which also have 2c-2e C−Au, N−Au, and B−Au bonds.[11,12] The compounds containing the hypercoordinated trigonal−bipyramidal $C(AuPPh_3)_5^+$ and octahedral $C(AuPPh_3)_6^{2+}$ cations are examples of interesting species with C−$AuPPh_3$ bonds.[12b] Theoretical studies of model systems $BH_n(AuPH_3)_m^k$, where $n + m = 3$ or 4 and charge k is -2, ..., $+1$,[12c] and model complexes $[(LAu)_6X_m]^{m+}$, $[(LAu)_5X_m]^{(m-1)+}$, and $[(LAu)_4X_m]^{(m-2)+}$ [with central atoms X_1 = B, X_2 = C, and X_3 = N and ligands L = PH_3 or $P(CH_3)_3$],[12d] where the authors analyzed the importance of Au−PR_3 interactions for the stability of these systems, have also been published. Pure XAu_n^{m+} clusters have been theoretically studied[12e] for the purpose of understanding the influence of Au−PR_3 interactions on chemical bonding in $X(AuPPh_3)_n^{m+}$ systems. The synthesis and characterization of the B-centered Au cluster in the $[(Cy_3P)B((AuPPh_3)_4]^+BF_4^-$ salt have also been reported.[12f] There are also several reports on gold diboride AuB_2 compounds, which have hexagonal layers of B atoms with Au atoms in between.[12g−k]

Our work on the $B_xAu_x^{2-}$ *closo*-auroboranes was inspired by the recent discovery of the Au−H analogy in several binary Au-containing clusters.[13] It was first demonstrated that $SiAu_4$ and $SiAu_n$ (n = 2 and 3) have structures and bonding similar to the silanes SiH_4 and SiH_n, respectively.[13a] The Si_2Au_n (n = 2 and 4) clusters were subsequently shown to be analogous to Si_2H_n (n = 2 and 4).[13b] We have recently found that the B−Au bonds in the $Au_2B_7^-$ cluster[13c] are also covalent and similar to the B−H bonds in the $B_7H_2^-$ cluster.[14]

On the basis of the Au−H analogy, we conjectured that the *closo*-auroboranes $B_xAu_x^{2-}$ could be viable new building blocks in chemistry. To test this idea, we performed quantum chemical calculations using hybrid density functional theory (DFT) method B3LYP,[15] as implemented in *NWChem 4.7*[16] and *Gaussian 03*[17] with three types of basis sets using also pseudopotential on Au: (1) LANL2DZ[18] on B and Au (B3LYP/LANL2DZ); (2) aug-cc-pvTZ[19] on B and Stuttgart pseudopotential and basis set[20] on Au (B3LYP/B/aug-cc-pvTZ/Au/Stuttgart); (3) cc-pvTZ[19] on B and Stuttgart pseudopotential and basis set on Au (B3LYP/B/cc-pvTZ/Au/Stuttgart). We optimized geometry and calculated frequencies for $B_xH_x^{2-}$ and $B_xAu_x^{2-}$ ($x = 5-12$) at B3LYP/LANL2DZ, $B_xH_x^{2-}$ ($x = 5-8$) at B3LYP/B/H/aug-cc-pvTZ, $B_xH_x^{2-}$ ($x = 9-12$) at B3LYP/B/H/cc-pvTZ, $B_xAu_x^{2-}$ ($x = 5-8$) at B3LYP/B/aug-cc-pvTZ/Au/Stuttgart, and $B_xAu_x^{2-}$ ($x = 9-12$) at B3LYP/B/cc-pvTZ/Au/Stuttgart levels of theory. Optimized geometries, harmonic frequencies, total energies, and other molecular properties of calculated species are summarized in the Supporting Information. B3LYP/LANL2DZ calculations have been performed at Utah State University using the *Gaussian 03* program. B3LYP/B/H/aug-cc-pvtz, B3LYP/B/H/cc-pvtz, B3LYP/B/aug-cc-pvtz/Au/Stuttgart, and B3LYP/B/cc-pvtz/Au/Stuttgart calculations have been performed at the Environmental Molecular Sciences Laboratory facility at Pacific Northwest National Laboratory using the *NWChem* program. The B3LYP results for $B_6Au_6^{2-}$ were also compared with other DFT functionals and ab initio calculations to validate the methods used. Preliminary global minimum searches for the $B_5Au_5^{2-}$ and $B_6Au_6^{2-}$ clusters were performed using CPMD simulated annealing via the plane-wave DFT code of *NWChem*. With various starting geometries and annealing temperatures, we did not find any energetically more stable structures. While a few structures of $B_5Au_5^{2-}$ and $B_6Au_6^{2-}$ clusters with low symmetry and Au−Au interactions were found to be lower in energy at the B3LYP level of theory than the deltahedral structures, they are significantly higher at the MP2 level of theory, indicating that the structures in Figure 1 are likely to be the global minima.

Selected geometric parameters for $B_xH_x^{2-}$ and $B_xAu_x^{2-}$ ($x = 5-12$) calculated at our highest level of theory are summarized in Figure 1, with Cartesian coordinates of all of these species collected in the Supporting Information.

Experimental geometries for the *closo*-borane $B_xH_x^{2-}$ dianions from crystal data are available for $x = 6$ and $8-12$. Our theoretical B−B and B−H distances for the free $B_xH_x^{2-}$ dianions agree within 0.08 Å, with the corresponding values for the same dianions in crystals. Similarly, our Au−B distances (2.056−2.072 Å) are in reasonable agreement with the crystal Au−B distance (2.16−2.19 Å) in the $[(Cy_3P)B((AuPPh_3)_4]^+BF_4^-$ salt.[12f]

According to our calculations using the B3LYP method with the largest basis sets, the *closo*-auroboranes $B_xAu_x^{2-}$

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(10) *Gold: Progress in Chemistry, Biochemistry and Technology*; Schmidbaur, H., Ed.; Wiley: Chichester, U.K., 1999; and references cited therein.

(11) Lauher, J. W.; Wald, K. *J. Am. Chem. Soc.* **1981**, *103*, 7648.

(12) (a) Scherbaum, F.; Grohmann, A.; Muller, G.; Schmidbaur, H. *Angew. Chem., Int. Ed.* **1989**, *28*, 463. (b) Grohmann, A.; Riede, J.; Schmidbaur, H. *Nature* **1990**, *345*, 140. (c) Tamm, T.; Pyykkö, P. *Theor. Chem. Acc*. **2000**, *103*, 399. (d) Häberlen, O. D.; Schmidbaur, H.; Rösch, N. *J. Am. Chem. Soc.* **1994**, *116*, 8241. (e) Pyykkö, P.; Zhao, Y. *Chem. Phys. Lett.* **1991**, *177*, 103. (f) Blumenthal, A.; Beruda, H.; Schmidbaur, H. *J. Chem. Soc., Chem. Commun.* **1993**, 1005. (g) Shein, I. R.; Medvedeva, N. I.; Ivanovski, A. L. *Phys. Solid State* **2001**, *43*, 2213. (h) Yang, F.; Han, R. S.; Tong, N. H.; Guo, W. *Chin. Phys. Lett*. **2002**, *19*, 1336. (i) Parvin, F.; Islam, A. K. M. A.; Islam, F. N. *Solid State Commun*. **2004**, *130*, 567. (j) Kwon, S. K.; Min, B. I.; Youn, S. J.; Kim, K. S. *J. Korean Phys. Soc*. **2005**, *46,* L1295. (k) Obrowski, W. *Naturwissenschaften* **1961**, *48*, 428.

(13) (a) Kiran, B.; Li, X.; Zhai, H. J.; Cui, L. F.; Wang, L. S. *Angew. Chem., Int. Ed*. **2004**, *43*, 2125. (b) Li, X.; Kiran, B.; Wang, L. S. *J. Phys. Chem. A* **2005**, *109*, 4366. (c) Zhai, H. J.; Wang, L. S.; Zubarev, D. Yu.; Boldyrev, A. I. *J. Phys. Chem. A* **2006**, *110*, 1689.

(14) Alexandrova, A. N.; Koyle, E.; Boldyrev, A. I. *J. Mol. Mod.* **2005**, published online.

(15) (a) Parr, R. G.; Yang, W. *Density-functional theory of atoms and molecules*; Oxford University Press: Oxford, U.K., 1989. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (c) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B* **1992**, *46*, 6671.

(16) Aprà, E.; et al. (see complete reference in the Supporting Information). *NWChem, A Computational Chemistry Package for Parallel Computers*, version 4.7; Pacific Northwest National Laboratory: Richland, WA, 2005.

(17) Frisch, M. J.; et al. (see complete reference in the Supporting Information). *Gaussian 03*, revision A.1; Gaussian, Inc.: Pittsburgh, PA, 2003.

(18) Hay, P. J.; Wadt, J. *J. Chem. Phys*. **1985**, *82*, 299.

(19) Kendall, R. A.; Dunning, T. H., Jr. *J. Chem. Phys.* **1992**, *96*, 6796.

(20) (a) Dolg, M.; Wedig, U.; Stoll, H.; Preuss, H. *J. Chem. Phys*. **1987**, *86*, 866. (b) Martin, J. M. L.; Sundermann, A. *J. Chem. Phys*. **2001**, *114*, 3408.

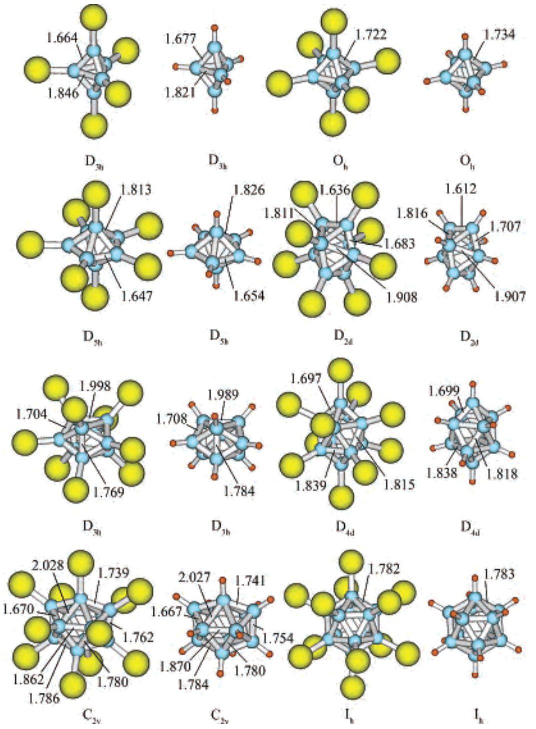

Figure 1. Optimized geometric structures of $B_xH_x^{2-}$ and $B_xAu_x^{2-}$ (x = 5−12) with selected B−B distances in angstroms (yellow, Au; blue, B; orange, H). See the Supporting Information.

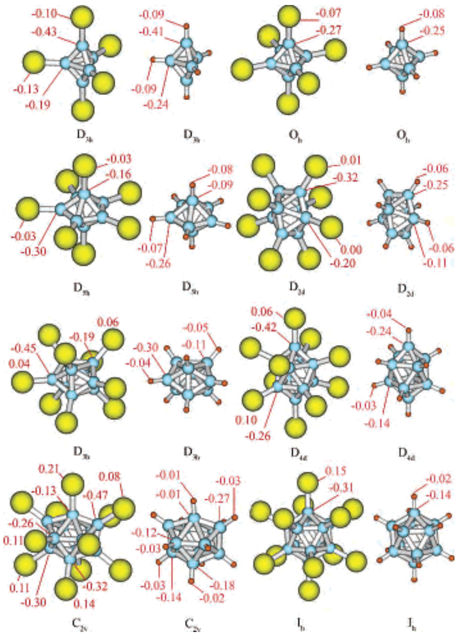

Figure 2. Calculated natural bond effective atomic charges in |e| (at B3LYP/LANL2DZ) for $B_xH_x^{2-}$ and $B_xAu_x^{2-}$ (x = 5−12).

with x = 5−12 have minimal energy structures completely identical with those of the corresponding $B_xH_x^{2-}$ species. The B−B bond lengths for the auroboranes $B_xAu_x^{2-}$ are indeed very similar to those of the corresponding boranes $B_xH_x^{2-}$ (Figure 1). The shortest Au−Au distances in $B_xAu_x^{2-}$ decrease slightly with increasing x from 4.56 Å in $B_5Au_5^{2-}$ to 3.95 Å in $B_{12}Au_{12}^{2-}$, but they are still significantly larger than the equilibrium Au−Au distance (2.47 Å) in Au_2 or the Au−Au distance (2.884 Å) in bulk Au, indicating that there is no direct Au−Au bonding in the *closo*-auroboranes. The shortest Au−Au distances in $B_xAu_x^{2-}$ are also outside the range of 3.00 ± 0.25 Å for aurophilic interactions,[8i] suggesting that the Au−B bonding, analogous to the B−H bonding in the pure *closo*-boranes and the Si−Au bonding in the Si/Au binary clusters,[13a,b] dominates in the $B_xAu_x^{2-}$ molecules. While it is nearly impractical to prove if these high-symmetry minimum structures are the most stable among all of the possible structures, it is conceivable that the *closo*-auroboranes $B_xAu_x^{2-}$ might be made if the synthesis starts with the cage boranes or their derivatives.

To further elucidate the analogy between $B_xAu_x^{2-}$ and $B_xH_x^{2-}$, we calculated the effective atomic charges using natural bond analysis (Figure 2).

We found that the atomic charges on Au and H in every pair of $B_xH_x^{2-}$ and $B_xAu_x^{2-}$ dianions are indeed very similar, although the Au−B bonds are slightly more polar than the B−H bonds. Thus, the covalent B−Au bonding in the *closo*-auroboranes is indeed analogous to the B−H covalent bonds in $B_xH_x^{2-}$, indicating that Au indeed mimicks H in $B_xAu_x^{2-}$. The relativistic effects account for the covalent character of the B−Au bonds.[21]

The present research suggests that the *closo*-auroborane dianions can be viable new building blocks in chemistry. We expect that $B_xAu_x^{2-}$ clusters may undergo catenation in the solid state and thus may require ligand protection, such as the PPh_3 groups. While it is hard for us to speculate if Au−B species without donor ligand protection can be isolated in the condensed phase, we believe that $B_x(AuPPh_3)_x^{2-}$ would be the most viable species to be synthesized in the condensed phase. The synthesis and characterization of the B-centered Au cluster in the $[(Cy_3P)B((AuPPh_3)_4]^+BF_4^-$ salt[12f] provide additional hope that such a synthesis might be feasible. The Au atoms in the *closo*-auroboranes represent highly atomically dispersed Au and may potentially exhibit novel catalytic and chemical properties.

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Supporting Information Available: Complete references for ref 16 and 17 and tables of optimized coordinates, harmonic frequencies, and other calculated molecular properties for $B_xAu_x^{2-}$ and $B_xH_x^{2-}$ (x = 5−12). This material is available free of charge via the Internet at http://pubs.acs.org.

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[21] Pyykkö, P. *Angew. Chem., Int. Ed.* **2004**, *43*, 4412.