Hf$_3$ Cluster Is Triply (σ-, π-, and δ-) Aromatic in the Lowest D_{3h}, ^{1}A$_1'$ State

Boris B. Averkiev and Alexander I. Boldyrev*

Department of Chemistry and Biochemistry, Utah State University, 0300 Old Main Hill, Logan, Utah 84322

Received: September 18, 2007; In Final Form: October 30, 2007

The extensive search for the global minimum structure of Hf$_3$ at the B3LYP/LANL2DZ level of theory revealed that D_{3h} ^{3}A$_2'$ (1a$_1'^2$1a$_2''^2$1e$'^4$2a$_1'^2$1e$''^2$) and D_{3h} ^{1}A$_1'$ (1a$_1'^2$2a$_1'^2$1e$'^4$1a$_2''^2$3a$_1'^2$) are the lowest triplet and singlet states, respectively, with the triplet state being the lowest one. However, at the CASSCF(10,14)/Stuttgart+2f1g level of theory these two states are degenerate, indicating that at the higher level of theory the singlet state could be in fact the global minimum structure. The triplet D_{3h} ^{3}A$_2'$ (1a$_1'^2$1a$_2''^2$1e$'^4$2a$_1'^2$1e$''^2$) structure is doubly (σ- and π-) aromatic and the singlet D_{3h} ^{1}A$_1'$ (1a$_1'^2$2a$_1'^2$1e$'^4$1a$_2''^2$3a$_1'^2$) structure is the first reported triply (σ-, π-, and δ-) aromatic system.

In recent years the concepts of aromaticity and antiaromaticity have been advanced beyond the framework of organic chemistry. In particular, aromaticity and antiaromaticity have been extended into organometallic compounds with cyclic cores of metal atom[1] and into all-metal clusters.[2] It has been shown that main group metal clusters, in which the chemical bonding involves only s-AOs and p-AOs, may possess multiple aromaticity (σ- and π-), multiple antiaromaticity (σ- and π-), and conflicting aromaticity (σ-aromaticity and π-antiaromaticity or σ-antiaromaticity and π-aromaticity).[2c] In the transition metal clusters in which d-orbitals are involved in chemical bonding σ-tangential (σ_t-), σ-radial (σ_r-), π-tangential (π_t-), π-radial (π_r-), and δ-aromaticity/antiaromaticity could occur. In this case, there can be triple (σ-, π-, and δ-) aromaticity, triple (σ-, π-, and δ-) antiaromaticity, and a variety of conflicting aromaticities (simultaneous σ-aromaticity, π-aromaticity, and δ-antiaromaticity; σ-aromaticity, π-antiaromaticity, and δ-aromaticity; σ-antiaromaticity, π-aromaticity, and δ-aromaticity; σ-aromaticity, π-antiaromaticity, and δ-antiaromaticity; σ-antiaromaticity, π-aromaticity, and δ-antiaromaticity; σ-antiaromaticity, π-antiaromaticity, and δ-aromaticity).

Aromaticity in transition metal systems has been already discussed in the literature.[2−12] King[3] and Li[4] have considered aromaticity in transition metal oxides due to metal−metal interactions via M−O−M bridges. Kuznetsov et al.[5] have shown that the Hg$_4^{6-}$ cluster, which is a building block of the Na$_3$Hg$_2$ amalgam, is aromatic similarly to the all-metal aromatic Al$_4^{2-}$ unit.[2a] Tsipis et al.[6] explained the planar structures of cyclic hydro-coinage metal compounds on the basis of their aromatic character. Alexandrova et al.[7] suggested the presence of aromaticity in the Cu$_3$C$_4^-$ cluster. Datta et al.[8] used d-orbital aromaticity to explain the metal ring structure in tiara-like nickel thiolates. Aromaticity in square-planar coinage metal clusters was discussed by Wannere et al.[9] and Lin et al.[10] The claim of d-aromaticity in the square-planar coinage metal clusters[9] was questioned by Lin et al.,[10] who showed that the completely filled d orbitals do not play any significant role in the bonding in these clusters. Instead, aromaticity in these systems comes primarily from σ bonding interactions of the valence s electrons. Recently, Huang et al.[11] demonstrated in the joint experimental and theoretical study the presence of d-orbital aromaticity in 4d and 5d transition metal oxide clusters, Mo$_3$O$_9^{2-}$ and W$_3$O$_9^{2-}$. In these clusters d-orbitals form σ-aromatic canonical molecular orbital. It was recently shown by Zhai et al.[12] that the Ta$_3$O$_3^-$ cluster possesses an unprecedented multiple (π and δ) aromaticity, which is responsible for the metal−metal bonding and the perfect triangular Ta$_3$ framework. However, this cluster does not possess σ-aromaticity, because the bonding from the delocalized 3a$_1'$-HOMO-3 is canceled by the antibonding contributions from the 4e′-HOMO.[12] So far, there are no any reported systems in the literature, that would have all three (σ-, π-, and δ-) types of aromaticity/antiaromaticity.

We conjectured that the Hf$_3$ cluster could possess triple (σ-, π-, and δ-) aromaticity, because Hf has the most diffuse valence orbitals out of all triatomic clusters of group IV thus providing good orbital overlap. Also, in the singlet D_{3h}, ^{1}A$_1'$ state this cluster may use all its six d-electrons to populate completely bonding delocalized σ-MO (2a$_1'$), π-MO (1a$_2''$), and δ-MO (3a$_1'$) in the 1a$_1'^2$2a$_1'^2$1e$'^4$1a$_2''^2$3a$_1'^2$ electronic configuration. These three MOs would render σ-, π-, and δ-aromaticity just like the completely bonding π-delocalized MO in C$_3$H$_3^+$ renders π-aromaticity in C$_3$H$_3^+$. However, this triply aromatic electronic state might not necessarily be the lowest state. It is known in chemistry that usually several σ-MO should be occupied, before π-bonding orbitals start to fill up. For example, in C$_3$H$_3^+$ (valence electronic configuration 1a$_1'^2$1e$'^4$2a$_1'^2$2e$'^4$1a$_2''^2$), the completely bonding π-MO (1a$_2''^2$) is occupied after the entire set of σ-MOs (1a$_1'^2$1e$'^4$2a$_1'^2$2e$'^4$). Thus, completely bonding δ-MO in Hf$_3$ could be occupied after the sets of σ- and π-MOs, and the triply aromatic state might not be among low-lying states.

To test our conjecture, we initially performed an extensive search for the Hf$_3$ global minimum for singlet, triplet, and quintet states at the B3LYP level of theory using the LANL2DZ pseudo-potential and basis set (B3LYP/LANL2DZ). We recalculated

Letters

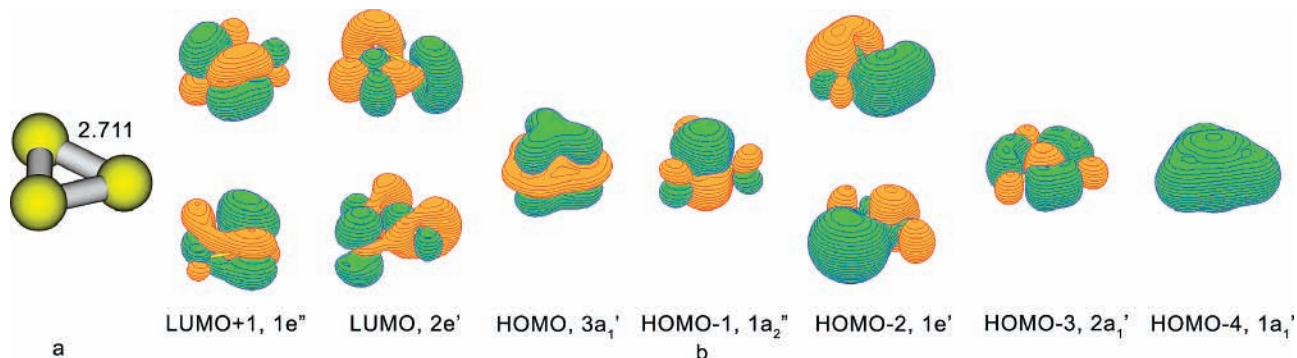*J. Phys. Chem. A, Vol. 111, No. 50, 2007* **12865**

Figure 1. (a) Structure of Hf$_3$ D_{3h}, $^1A_1{}'$ optimized at the B3LYP/Stuttgart+2f1g level of theory. (b) Valence molecular orbitals at the B3LYP/Stuttgart+2f1g level of theory.

the global minimum structure and the seven lowest isomers at the B3LYP level of theory using the Stuttgart+2f1g pseudo-potential and basis set (B3LYP/Stuttgart+2f1g) (see Supporting Information for additional results and details of theoretical calculations). At this level of theory we found that the lowest isomer of Hf$_3$ has the triangular D_{3h} $^3A_2{}'$ structure with the $1a_1{}'^2 1a_2{}''^2 1e'^4 2a_1{}'^2 1e''^2$ valence electronic configuration. The lowest singlet state with the triangular D_{3h} $^1A_1{}'$ ($1a_1{}'^2 2a_1{}'^2-1e'^4 1a_2{}''^2 3a_1{}'^2$) structure was found to be 9.2 kcal/mol (B3LYP/Stuttgart+2f1g) higher in energy than the triplet D_{3h} $^3A_2{}'$ structure. The B3LYP/CEP-121G calculations of the Hf$_3$ cluster have been reported by Jin et al.[13] They concluded that the singlet D_{3h} $^1A_1{}'$ state is the global minimum for Hf$_3$ in contradiction to our B3LYP results. We recalculated the D_{3h} $^3A_2{}'$ and D_{3h} $^1A_1{}'$ structures of Hf$_3$ at the B3LYP/CEP-121G level of theory and found the triplet state to be more stable than the singlet state by 8.2 kcal/mol. Apparently Jin et al.[13] missed the lowest triplet state. However, the B3LYP method could overestimate stability of triplet states over singlet states. To test this, we performed a series of CASSCF calculations at the B3LYP/Stuttgart+2f1g geometries. Because the CASSCF calculations are based on the restricted open shell Hartee−Fock (ROHF) method, we first calculated both D_{3h} $^3A_2{}'$ and D_{3h} $^1A_1{}'$ structures at the ROHF/Stuttgart+2f1g level of theory. The D_{3h} $^3A_2{}'$ triplet state was found to be 31.3 kcal/mol lower in energy than the D_{3h} $^1A_1{}'$ singlet state. However, the energy difference dramatically decreased to 7.2 kcal/mol at the CASSCF(8,8)/Stuttgart+2f1g level of theory and even further to 0.5 kcal/mol at CASSCF(10,14)/Stuttgart+2f1g. Thus, the singlet state might become the ground state for the Hf$_3$ cluster, as the number of active electrons and active orbitals is further increased. However, such calculations are beyond our computational abilities. Our B3LYP/LANL2DZ, B3LYP/Stuttgart+2f1g, CASSCF(8,8)/Stuttgart+2f1g, and CASSCF(10,14)/Stuttgart+2f1g calculations have been performed using the Gaussian 03 program.[14] The high level calculations for Hf$_3$ have been performed by Dai et al.[15] According to their MRCISD/4s4p3d calculations the triplet C_{2v}, $^3A_2$ state is the most stable one with the lowest singlet C_{2v}, $^1A_1$ state being 2.5 kcal/mol higher in energy. However these two states were not the lowest triplet and singlet states in our B3LYP/Stuttgart+2f1g calculations (see Supporting Information). To test the influence of relativistic effects on the singlet−triplet splitting, we performed additional calculations using the B3LYP (with the all electron TZ2P Slater basis set) level of theory (B3LYP/TZ2P) and the B3LYP/TZ2P plus zero-order regular approximation (ZORA), which is the scalar relativistic approximation (B3LYP/ZORA/TZ2P) at the optimized B3LYP/Stuttgart+2f1g geometries. Our B3LYP/TZ2P and B3LYP/ZORA/TZ2P calculations have been performed

using the ADF program.[16] The triplet D_{3h} $^3A_2{}'$ state was found to be 3.4 kcal/mol (B3LYP/TZ2P) and 8.4 kcal/mol (B3LYP/ZORA/TZ2P) more stable than the D_{3h} $^1A_1{}'$ state. Thus, the scalar relativistic effects stabilize the triplet state more than the singlet, though the stabilization effect is rather small (5.0 kcal/mol). The influence of spin−orbit coupling on the singlet−triplet splitting in Hf$_3$ was studied by When Dai et al.[15] They found that the triplet state is stabilized more than singlet due to the state mixing. Because the multiconfigurational effects favor the singlet over the triplet and relativistic effects favor the triplet over the singlet, it is difficult at this point to determine with certainty if the Hf$_3$ cluster is a singlet or a triplet in its ground electronic state. However, if the singlet state is not the ground state it is certainly a low-lying excited state. Indeed, Wang et al.[17] stated that Raman spectra of Hf$_3$ are too complicated to be explained by a single electronic state and they suggested that Hf$_3$ has a number of low-lying electronic states. We also would like to point out that in spin−orbit calculations by Dai et al.[15] the largest contribution of the triplet state to the lowest singlet state does not exceed 0.2% and thus our chemical bonding analysis of the triple aromatic nature of the lowest singlet state is not significantly affected by the spin−orbit effects.

The singlet D_{3h} $^1A_1{}'$ structure is indeed a triply (σ-, π-, and δ-) aromatic system. The $1a_2{}''$-MO is a circularly delocalized π-MO (similar to the $1a_2{}''$-MO in $C_3H_3{}^+$, that renders π-aromaticity in $C_3H_3{}^+$), the $2a_1{}'$-MO is a circularly delocalized σ-MO, and the $3a_1{}'$-MO is a circularly delocalized δ-MO (Figure 1). All these bonding MOs are formed by d-AOs of Hf, and thus we have an example of triple d-aromaticity. Pictures of the molecular orbitals are made using Molden 3.4 program.[18]

We also calculated nuclear independent chemical shifts (NICS$_{zz}$)[19] to probe aromaticity in Hf$_3$. We found that NICS$_{zz}$ is large and negative at the center of the cluster and quickly diminishing above the plane: NICS$_{zz}$ = −41.5 ppm (z = 0.0 Å), NICS$_{zz}$ = −23.0 ppm (z = 0.5 Å), and NICS$_{zz}$ = +4.0 ppm (z = 1.0 Å), thus providing additional evidence of multiple aromaticity in Hf$_3$ (D_{3h}, $^1A_1{}'$). The triangular D_{3h} $^3A_2{}'$ structure with the $1a_1{}'^2 1a_2{}''^2 1e'^4 2a_1{}'^2 1e''^2$ electronic configuration is a doubly (σ- and π-) aromatic state with two σ-electrons and four π-electrons. Two σ-electrons render σ-aromaticity according to the $4n + 2$ rule for the singlet coupling of electrons and four π-electrons render π-aromaticity according to the $4n$ rule for the triplet coupling of electrons. Thus, the competition for being the global minimum in Hf$_3$ occurs between the singlet triply (σ-, π-, and δ-) aromatic D_{3h} $^1A_1{}'$ ($1a_1{}'^2 2a_1{}'^2 1e'^4 1a_2{}''^2 3a_1{}'^2$) state and the triplet doubly (σ- and π-) aromatic D_{3h} $^3A_2{}'$ ($1a_1{}'^2 1a_2{}''^2 1e'^4 2a_1{}'^2 1e''^2$) state.

In our highest (CASSCF(10,14)/Stuttgart+2f1g) multi-configurational treatment the occupation numbers were found

to be $1a_1'^{2.00}2a_1'^{1.86}1e'^{3.82}1a_2''^{1.87}3a_1'^{1.74}2e'^{0.30}$ $1e''^{0.13}3e'^{0.14}$-$2e''^{0.13}1a_2'^{0.02}$. One can see that about 0.3 |e| have been promoted from $3a_1'$ δ-HOMO into $2e'$ σ-LUMO. That means that δ-aromaticity is reduced at the multiconfigurational level of theory because the $3a_1'$ δ-HOMO lost some electron density and that σ-aromaticity is reduced too at the same level of theory because bonding/antibonding $2e'$ σ-LUMO gained some electron density compared to the pure one electron treatment. Partial promotion from δ-HOMO into $2e'$ σ-LUMO occurs to reduce electron density and electron repulsion at the center of the cluster due to the presence of four electrons on completely bonding HOMO and HOMO−3. In spite of some multiconfigurational nature of the wave function, we believe that our qualitative assignment of the singlet D_{3h} $^1A_1'$ structure of Hf$_3$ as the triply aromatic is still valid, because a rather small amount of electron density from HOMO to LUMO was promoted and the Hartree−Fock configuration (with the coefficient 0.842) is still dominant in the CASSCF(10,14)/Stuttgart+2f1g expansion.

In summary, in the current communication we presented theoretical evidence that the lowest singlet D_{3h} $^1A_1'$ structure of Hf$_3$ is the first example of a triply (σ-, π-, and δ-) aromatic system. We believe that transition metal systems with triple antiaromaticity and all types of conflicting aromaticity outlined in the Introduction will be identified soon. Most importantly, we hope that our work would stimulate theoretical analysis of chemical bonding in numerous known chemical compounds with metal clusters at the center (such as carbonyls of transition metals) with the goal to probe if these systems are in fact aromatic, antiaromatic or they have conflicting aromaticity and how this affects their stability and reactivity.

Supporting Information Available: Optimized alternative structures, energies, and detailed theoretical description of our calculations with the complete ref 14. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Robinson, G. H. *Acc. Chem. Res.* **1999**, *32*, 773.

(2) (a) Li, X.; Kuznetsov, A. E.; Zhang, H. F.; Boldyrev, A. I.; Wang, L. S. *Science* **2001**, *291*, 859. (b) Kuznetsov, A. E.; Birch, K. A.; Boldyrev, A. I.; Li, X.; Zhai, H.-J.; Wang, L. S. *Science* **2003**, *300*, 622. (c) Boldyrev, A. I.; Wang, L. S. *Chem. Rev.* **2005**, *106*, 3716 and references therein. (d) Tsipis, C. A. *Coord. Chem. Rev.* **2005**, *249*, 2740 and references therein.

(3) King, R. B. *Inorg. Chem.* **1991**, *30*, 4437.

(4) Li, J. *J. Cluster Sci.* **2002**, *13*, 137.

(5) Kuznetsov, A. E.; Corbett, J. D.; Wang, L. S.; Boldyrev, A. I. *Angew. Chem. Int. Ed.* **2001**, *40*, 3369.

(6) Tsipis, A. C.; Tsipis, C. A. *J. Am. Chem. Soc.* **2003**, *125*, 1136.

(7) Alexandrova, A. N.; Boldyrev, A. I.; Zhai, H.-J.; Wang, L. S. *J. Phys. Chem. A* **2005**, *109*, 562.

(8) Datta, A.; John, N. S.; Kulkarni, G. U.; Pati, S. K. *J. Phys. Chem. A* **2005**, *109*, 11647.

(9) Wannere, C. S.; Corminboeuf, C.; Wang, Z.-X.; Wodrich, M. D.; King, R. B.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **2005**, *127*, 5701.

(10) Lin, Y.-C.; Sundholm, D.; Juselius, J.; Cui, L.-F.; Zhai, H.-J.; Wang, L. S. *J. Phys. Chem. A* **2006**, *110*, 4244.

(11) Huang, X.; Zhai, H.-J.; Kiran, B.; Wang, L. S. *Angew. Chem. Int. Ed.* **2005**, *44*, 7251.

(12) Zhai, H.-J.; Averkiev, B. B.; Zubarev, D. Yu.; Wang, L. S.; Boldyrev, A. I. *Angew. Chem. Int. Ed.* **2007**, *46*, 4277.

(13) Jin, P. C.; Han, B.; Dai, Z. W.; Wu, Z. J. *J. Mol. Struct. THEOCHEM* **2004**, *680*, 1.

(14) Frisch, M. J.; et al. *Gaussian 03*, revision D.01; Gaussian, Inc.: Wallingford, CT, 2004.

(15) Dai, D.; Roszak, S.; Balasubramanian, K. *Chem. Phys. Lett.* **1999**, *308*, 495.

(16) ADF2007.01; SCM, Theoretical Chemistry, Vrije Universiteit: Amsterdam, The Netherlands, 2007.

(17) Wang, H.; Hu, Z.; Haouari, H.; Craig, R.; Liu, L.; Lambardi, J. R.; Lindsay, D. M. *J. Chem. Phys.* **1997**, *106*, 8339.

(18) MOLDEN3.4. Schaftenaar, G. MOLDEN3.4, CAOS/CAMM Center, The Netherlands, 1998.

(19) (a) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317. (b) Fowler, P. W.; Steiner, E. *Mol. Phys.* **2000**, *98*, 945. (c) Steiner, E.; Fowler, P. W.; Jenneskens, L. W. *Angew. Chem. Int. Ed.* **2001**, *40*, 362.