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Coaxial alkaline-earth dimetal units sandwiched between hydrosilver compounds: A DFT Study

Jia Zhou, Fei Xiao, Zhi-Pan Liu, Kang-Nian Fan *

Shanghai Key Laboratory of Molecular Catalysis & Innovative Materials, Department of Chemistry, Center for Theoretical Chemical Physics, Fudan University, Shanghai 200433, China

Abstract

Density functional theory methods have been utilized to investigate the novel dicationic hydrosilver sandwich compounds, $[(Ag_nH_n)M_2]^{2+}$ ($n = 4$, 5; M = Be, Mg, and Ca). The two alkaline-earth metal atoms were found to form a single bond. The NBO analyses show that with the increase of ionic potential of the alkaline-earth metal, the positive charge diffuses more and more weakly. The hydrosilver rings do not change much except for a little departure of the hydrogen atoms. This series of dicationic complexes may be stabilized with the aid of strong electron acceptor and form one dimensional nanostructures.
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The decamethyldizincocene (η^5-Me$_5$C$_5$)$_2$Zn$_2$, which was obtained from the reaction of (η^5-Me$_5$C$_5$)$_2$Zn with Et$_2$Zn accidentally [1], has elementarily changed the classical concept of the sandwich compounds. The binuclear metallocenes, with two metal atoms being sandwiched between two cyclopentadienyl rings and the metal atom having a strong bond with each other, expand our current views and foresee a series of novel compounds of potential use. Stimulated by this pioneer work, some theoretical predictions were also carried out on the relevant derivatives, including the (C$_5$H$_5$)$_2$Cu$_2$ [2], (C$_5$H$_5$)$_2$Zn$_2$ [2], (C$_5$H$_5$)$_2$Ni$_2$ [2], and (C$_5$H$_5$)$_2$Be$_2$ [3], (C$_5$H$_5$)$_2$Mg$_2$ [3], (C$_5$H$_5$)$_2$Ca$_2$ [3]. On the other hand, cyclopentadienyl is not expected to be the only choice to stabilize the binuclear metal atoms. In particular, the concept of the aromaticity is no longer limited to the classic organic rings or even to nonmetals. The main group metal rings and related clusters have been well-investigated experimentally and theoretically [4]. Remarkably, the coinage metal elements have also been found to be able to form the M$_n$H$_n$ (M = Ag, Au and n = 3–6) rings with the clear aromaticity [5]. The metal–metal bond between the metal aromatic rings is really fascinating. Here, we present a systemic study to anticipate this series of compounds.

Two selected density functional theory (DFT) methods were employed in this study. One is B3LYP [6], which incorporate Becke's three parameter functional with the Lee, Yang, and Parr correlation functional, while the other is BP86 [7], which combines Becke's 1988 exchange functional with Perdew's 1986 correlation functional. The DZP basis sets for the hydrogen and alkaline-earth metals were 6-31G(d,p). For the transition metal silver, the basis sets LanL2DZ and the corresponding Los Alamos relativistic effective core potential (RECP) were used to take into account scalar relativistic effects, including mass velocity and Darwin correction. All the calculations were carried out with the Gaussian 03 program [8]. The ultrafine integration grid and the rigorous convergence criteria in the program were both applied for the reliable results. The natural bond orbital (NBO) analyses [9] had also been carried out to gain better insight into the bonding of these systems.

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* Corresponding author. Tel./fax: +86 21 65643977.
  E-mail address: knfan@fudan.edu.cn (K.-N. Fan).

The equilibrium geometries of the cyclic Ag_nH_n ($n = 4$, 5) molecules have been thoroughly investigated by Tsipis et al. [5]. Both structures are found to be energetic minima and exhibit a clear aromaticity. We also calculated the two structures with the methods mentioned above, and the results with two different functionals are all in good agreement with the previous study. We then investigated The $[(Ag_4H_4)M_2]^{2+}$ and $[(Ag_5H_5)M_2]^{2+}$ (M = Be, Mg, and Ca) complexes. The structures are showed in Figs. 1 and 2. The corresponding structural parameters are tabulated in
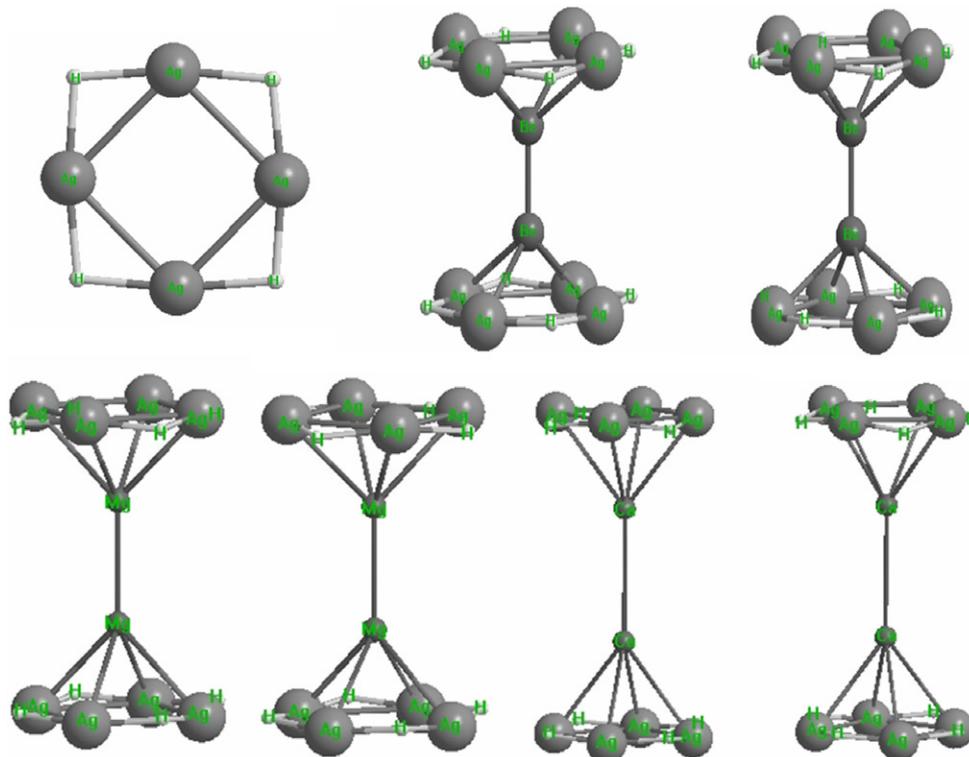

Fig. 1. Optimized structure of D_{4h} Ag_4H_4, and D_{4h} and D_{4d} $[(Ag_4H_4)M_2]^{2+}$ (M = Be, Mg, and Ca).
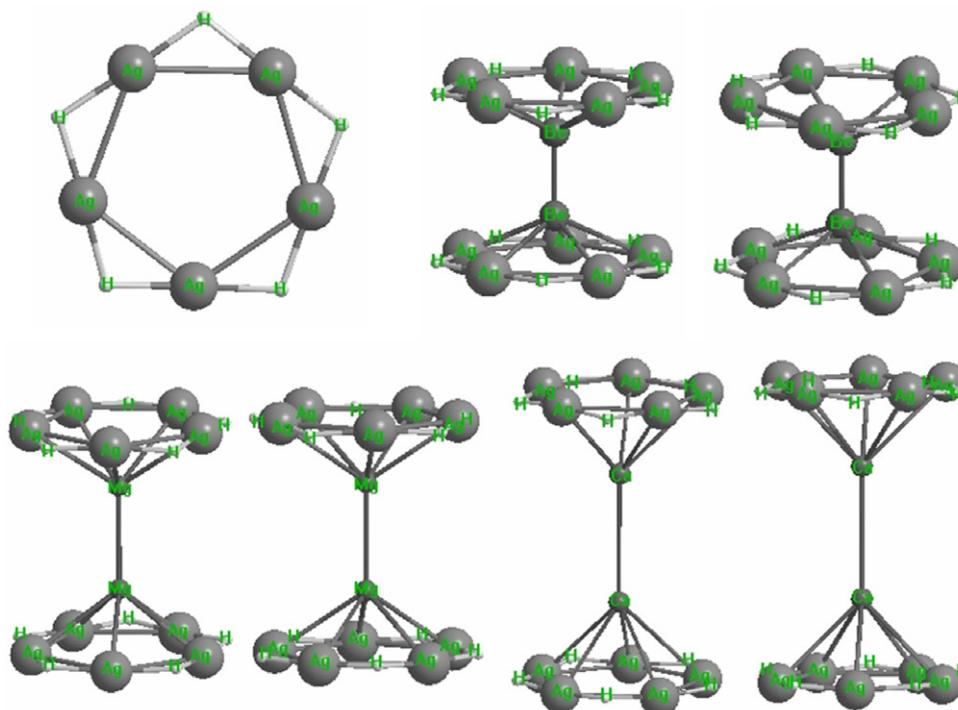
Fig. 2. Optimized structure of D_{5h} Ag_5H_5, and D_{5h} and D_{5d} $[(Ag_5H_5)M_2]^{2+}$ (M = Be, Mg, and Ca).

Tables 1 and 2, Supplementary material. The energy differences between the staggered (D_{4d}/D_{5d}) and the eclipsed (D_{4h}/D_{5h}) conformations are very small and within the 0.01 kcal/mol. It should been mentioned that some of our results have suspiciously low magnitude imaginary vibrational frequencies (smaller than $15i\,cm^{-1}$), which is a known DFT limitation because of the numerical integral procedure. We did not follow these imaginary eigenvectors to search other minima, but treat them as or at least very close to local minima[10].

For Ag_4H_4, the ring size increases when the alkaline-earth cation atoms inserting. The parameters of complexes with the two symmetries (D_{4d} and D_{4h}) nearly have the same value. The electronic properties calculated by B3LYP with the same basis set are listed in Table 3, Supplementary material. With the distance of the metal cation and hydrosilver ring increasing, the positive charge prefers the alkaline-earth sites. The Wiberg bond index (WBI) between the beryllium and hydrosilver ring is about 0.83, almost a single bond, while that in the calcium complex is only 0.23. The WBI between the center metal and metal is 0.567, 0.624, and 0.797 for beryllium, magnesium, and calcium, respectively. This indicates that there is a clear metal-metal single bond between the two alkaline-earth metal atoms, especially for the calcium atoms. The interaction between the beryllium and hydrosilver ring is obviously greater than those in the other two complexes. Thereby, the charge transfer between beryllium cation and hydrosilver is that significant, followed by magnesium and calcium cations. This trend has something with the different ionic potential (IP) of the alkaline-earth metal: the one with the high IP inclines to loose the electron and vice versa. As the result, the calcium gets one positive charge nearly, while the beryllium obtains less than a half.

The similar situation also happens to $[(Ag_5H_5)M_2]^{2+}$. The electronic properties with the same calculation as front are listed in Table 4, Supplementary material. The WBI between the beryllium and hydrosilver ring is about 0.93, almost a single bond, while the counterpart in the calcium complex is only 0.30. The WBI between the center metal and metal cation is 0.497, 0.535, and 0.728 for beryllium, magnesium, and calcium, respectively, somewhat smaller than those in the $[(Ag_4H_4)M_2]^{2+}$, which indicates that there is also a clear single bond between the two alkaline-earth metal cations but a little weaker. Since the ring radius grows, the inserted alkaline-earth metal cations do not have much influence on the hydrosilver ring, which could be seen from the changes of the ring size and the electron properties of the ring. The results of the two symmetries (D_{5d} and D_{5h}) are generally the same, but the beryllium complex has the exception. The ring size of the D_{5d} symmetry is a little larger than that of the D_{5h} symmetry. The properties of $[(Ag_5H_5)M_2]^{2+}$ with the three kinds of alkaline-earth metal follow the similar trend to the $[(Ag_4H_4)M_2]^{2+}$.

We further studied the frontier molecular orbitals of the two sandwich-type complexes. Fig. 3 displays the

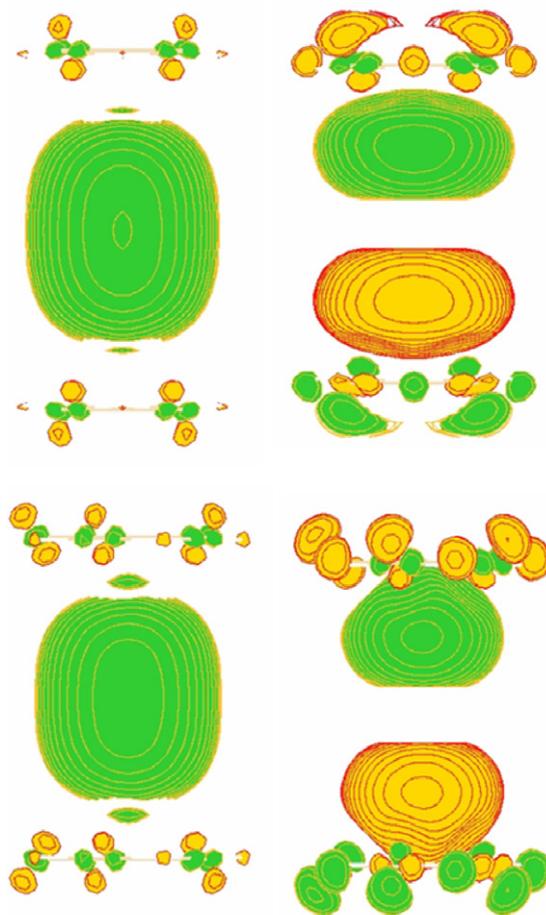Fig. 3. HOMO and LUMO for the D_{nh} $[(Ag_nH_n)M_2]^{2+}$ ($n = 4$, 5 and M = Be, Mg, and Ca).

frontier orbitals of the $[(Ag_4H_4)M_2]^{2+}$ and $[(Ag_5H_5)M_2]^{2+}$. The various alkaline-earth metal complexes have a very similar shape of the frontier molecular orbitals and distinction is only the orbitals energy. The highest occupied molecular orbital (HOMO) is mainly from the alkaline-earth metal s orbitals that form a clear metal–metal σ bond. By contrast, the lowest unoccupied molecular orbital (LUMO) is the corresponding metal–metal σ anti-bond. This finding implies the stability of this novel series of compounds.

In summary, we have presented DFT predictions that the alkaline-earth cations, including Be, Mg, and Ca, has a clear single bond in the new class of sandwich-type complexes. The NBO analyses show that the positive charge diffuses weakly with the center metal atomic number increasing, and this phenomenon is somewhat related with the ionic potential of the alkaline-earth metal. The hydrosilver ring still maintains perfect symmetry only with the hydrogen atoms a little departure. Our di-cationic complexes could be stabilized with the aid of strong electron acceptor and form one dimensional nanostructures. Both of these two investigations are in progress.

Acknowledgments

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.theochem.2007.01.006.

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