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Al_{12} and the Al@Al_{12} clusters

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The recent experimental characterization of the Al_{77} cluster by Ecker *et al.* [Nature **387**, 379 (1997)] detailed a fascinating onionlike structure whose inner core we report on here. The clusters Al_{12} and Al@Al_{12} have been studied in detail. Potential-energy surfaces have been examined using density-functional methodology and basis sets with effective core potentials. The stationary points located with this methodology were then further analyzed using full-electron basis sets of triple-zeta plus double polarization size. Two stationary points have been located on the Al_{12} surface, a staggered minimum of D_{5d} symmetry and a saddle point of Hessian order three in an eclipsed conformation with D_{5h} symmetry. The cationic, neutral, and anionic surfaces of Al@Al_{12} were explored. Structures similar to the Al_{12} stationary points were found for the anionic Al@$Al_{12}{}^{-}$ cluster though in this case the staggered minimum had icosahedral symmetry and the eclipsed stationary point was a true transition state. No atom-in-a-cage–type structure could be located for the cationic $Al_{13}{}^{+}$ cluster, but one minimum was found for the neutral. That C_1 minimum is in astonishing agreement with the core of Ecker's Al_{77} cluster having center-to-surface bond lengths that range from 2.635 to 2.850 Å and average 2.744 Å. [S1050-2947(98)02907-2]

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I. INTRODUCTION

The recent report of Ecker, Weckert, and Schnöckel [1] on the synthesis of a compound containing Al_{77} cluster units provided a fascinating view of a species exemplifying the intricacy of the crossover between molecular species and bulk metal. Indeed, Al_{77} represents one of the very early stages of the transition from the molecular to the bulk regime, since it contains one atom ''metallic'' in character, the central atom with coordination number 12, and the remaining 76 atoms located in increasingly molecularlike coordination spheres. In Ecker's cluster, the 77 atoms of aluminum are arranged in layers with one central atom covered by shells of 12, 44, and 20 atoms. The central atom is the only one coordinated to 12 others, but the arrangement is a distorted icosahedron, rather than cuboctahedral. The coordination number of the atoms in the other shells decreases from the center outward making a transition from the metallic center to a molecular surface.

Here we provide a detailed study of the central core of that Al_{77} cluster. First, we characterize the Al_{12} hollow cage, then examine the cationic, neutral, and anionic Al@Al_{12} clusters. By focusing on the core of Ecker's cluster, we describe a very small cluster that includes a ''metallic'' center atom and ''molecular'' atoms on the surface. Clearly, the synthesis of such a small atom-in-a-cage structure would be a very interesting development and our work here shows that for both the neutral and anionic cases, the formation of the Al@Al_{12} cluster is quite exothermic.

One experimental work detailing a compound with Al_{12} icosahedra has previously been published, that the work of Hiller *et al.* [2]. The icosahedra of that $K_2[Al_{12}i\mathrm{Bu}_{12}]$ compound were slightly distorted with bond lengths ranging from 2.679 to 2.696 Å. Despite the stability of this compound and the high interest in similar boron compounds, e.g., [3–5] no further experimental syntheses of related compounds have appeared until the work of Ecker *et al.* [1].

Two theoretical investigations related to this topic have appeared in the literature. The first of these calculates binding energies of $i\mathrm{Al}_{12}$, $i\mathrm{Cu@Al}_{12}$, and $i\mathrm{Al@Al}_{12}$, the building blocks of quasicrystals [6]. They reported maximum binding energies at center to vertex distances of 2.88 Å for $i\mathrm{Al@Al}_{12}$ and 2.66 Å for $i\mathrm{Al}_{12}$. The second [7] proposed the use of a general Tersoff potential for describing H, Al, and Sn clusters of up to 72 atoms. For the Al@Al_{12} cluster they reported average bond lengths ranging from 2.29 to 2.54 Å depending on the method used.

Thus we see that while the clusters of aluminum are capable of providing interesting insight into the evolution from molecular to metallic substances as demonstrated by the work of Ecker *et al.* [1], they remain relatively understudied. With this detailed report of the Al_{12} cage and the atom-in-a-cage Al@Al_{12} cluster we hope to spur on further experimental investigation into these interesting compounds.

II. METHODS

All geometries were fully optimized using the B3LYP gradient-corrected density-functional method [8–11] analytic gradients. As the potential surface was for many isomers rather flat with regards to change in geometry, the [opt =tight] option was used, meaning that internal forces were less than 0.000 015 hartree/bohr in all cases. Harmonic vibrational frequencies were determined by numerical differentiation of gradients.

The LanL2DZ basis set [12–14] composed of the Los Alamos effective core potential plus a double-ζ set of functions was used for initial calculations. However, as this set does not include *d* functions, it was necessary to add a set of five pure-angular-momentum *d* functions to this basis in order to properly describe the high-valency of the aluminum atoms. The exponent of the added set of *d* functions was 0.4.

In order to improve the determination of the relative energies of the various isomers, and to provide a more flexible

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basis set for the natural bond orbital (NBO) [15] analysis, the McLean-Chandler (12S9P/6S5P) basis set [16] augmented with two sets of five pure-angular-momentum *d* functions and one set of seven pure-angular-momentum *f* functions [6-311(2df)] was used. To this basis, a standard set of diffuse functions was added [6-311+(2df)] in order to provide a basis set capable of describing electron affinities with some confidence. For these single-point energy calculations, the geometries optimized at the B3LYP/LanL2DZ(d) level of theory were used.

All calculations were carried out with the GAUSSIAN94 package [17].

III. THE Al_{12} ISOMERS

A. The Al_{12} staggered isomer

The Al_{12} cluster is predicted to be a minimum on the B3LYP/LanL2DZ(d) potential-energy surface when the two rings of five aluminum atoms are in a staggered conformation. Thus the predicted equilibrium geometry is one of D_{5d} symmetry with two types of Al atoms, the ''peak'' atoms and the ''ring'' atoms. This configuration also leads to three types of bonds, ''peak-to-ring,'' ''ring,'' and ''ring-to-ring'' where ''ring'' refers to Al-Al bonds within the same ring and ''ring-to-ring'' refers to bonds across the molecular equator.

The two peak atoms have five equivalent Al-Al bonds. According to the B3LYP/LanL2DZ(d) level of theory, these bonds are predicted to be of length 2.743 Å. The shortest bonds within the cluster are the ring bonds with a predicted bond length of 2.681 Å, and the longest bonds are the ring-to-ring bonds at 2.847 Å. Thus, the average of the five bond lengths for each of the ring Al atoms is 2.760 Å, very close to the peak-to-ring bond length.

Hiller *et al.* reported the synthesis of a compound containing Al_{12} icosahedra in 1991 [2]. The unit formula for the crystal was $K_2[Al_{12}iBu_{12}]$. They also reported three different bond lengths, describing a structure only slightly distorted from icosahedral symmetry. The three bond lengths (determined by x-ray diffraction) found in their structure were 2.679(5) Å, 2.680(4) Å, and 2.696(5) Å [2], where the number in parentheses is the uncertainty in the last digit. Thus we see that our predictions are in reasonable agreement with the experimental findings, though there does exist more variation in our Al-Al bond lengths.

Vibrational frequency analysis did confirm that this structure is a minimum on the B3LYP/LanL2DZ(d) potential-energy surface. The predicted infrared harmonic vibrational frequencies range from a minimum of 61 cm^{-1} to a maximum of 330 cm^{-1}. The ''breathing'' mode of this structure has a frequency of 257 cm^{-1}.

The charge separation in this isomer is minimal. At the B3LYP/6-311(2df) level of theory, the reported Mulliken charges are very small indeed; the peak atoms have a negative charge of $-0.035e^-$ and the ring atoms a charge of $+0.008e^-$. The natural charge from the NBO analysis is also negative on the peak atoms but with a value of $-0.182e^-$, about five times greater than the Mulliken value. In either case, the separation of charge in this molecule is minimal.

B. The Al_{12} eclipsed isomer

A second isomer, this one of D_{5h} symmetry, was considered also. This stationary point on the B3LYP/LanL2DZ(d) potential energy surface is not a minimum, instead it is a saddle point of Hessian order three. Here the ring aluminum atoms are eclipsed. Again there are two types of atoms and three types of bonds. However, here there are only five ring-to-ring bonds rather than ten as in the staggered case.

The peak-to-ring bonds, predicted to have a length of 2.713 Å are 0.030 Å shorter than those of the minimum. The ring bond lengths of this isomer are 0.015 Å longer than those of the staggered minimum, but the ring-to-ring bonds that are the shortest Al-Al bonds found in either isomer, measuring 2.671 Å, are 0.146 Å shorter than their counterparts in the minimum. It must be remembered, though, that here there are only five, not ten, ring-to-ring bonds. The average bond length for the four bonds of the ring aluminum atoms is 2.694 Å, 0.066 Å shorter than the average of the five bonds of the ring atoms in the staggered minimum.

As mentioned earlier, this stationary point is not a minimum or a transition state, rather it is a saddle point of Hessian order three. The lowest of the three imaginary frequencies (at $39i$ cm^{-1}) does correlate to ring rotation leading directly to the staggered minimum. The other two imaginary frequencies are a degenerate pair which correlate to distortion.

Again, the Mulliken and natural charges disagree on the extent of charge separation, but both show the same polarization. According to the natural charges calculated at the B3LYP/6-311(2df) level of theory, there is a charge of $-0.217e^-$ on the two peak atoms and a positive charge of $+0.043e^-$ on the ring atoms.

Energetically, this stationary point lies 5.47 kcal/mol above the minimum according to the B3LYP/LanL2DZ(d)+ zero-point vibrational-energy correction level of theory. Applying the B3LYP/LanL2DZ(d) ZPVE correction to the B3LYP/6-311(2df) energy difference yields a final difference of 6.88 kcal/mol. Thus we see that while this large basis set does stabilize the minimum slightly more than it does the eclipsed stationary point, the LanL2DZ(d) basis set does a very good job of predicting relative energies for this system.

C. The effect of *d* functions

Aluminum atoms have no occupied *d* orbitals and thus the standard LanL2DZ basis set does not include *d* functions. This standard basis set was used in the preliminary investigation of the Al_{12} cluster and the results are both interesting and informative, demonstrating the importance of *d* functions even when no *d* orbitals are formally occupied.

The bond lengths predicted by the B3LYP/LanL2DZ level of theory are all longer than those predicted after *d* functions were added. For both isomers, the predicted peak-to-ring and ring bonds are approximately 0.09 Å longer when no *d* functions are present in the basis set. The ring-to-ring bonds, however, show significant differences between the two cases. Both sets are predicted to be longer in the absence of *d* functions, but the ten ring-to-ring bonds of the staggered isomer are 0.102 Å longer while the five ring-to-ring bonds of the eclipsed isomer are only 0.049 Å longer.

Even more interesting is that the d functions change the shape of the potential energy surface. When the unaugmented LanL2DZ basis set is used, it is the *staggered* isomer that is a saddle point of Hessian order three and the *eclipsed* isomer that is the minimum (though the lowest harmonic vibrational frequency has a value of only 21 cm^{-1}). Similarly, the eclipsed isomer lies 3.73 kcal/mol below the staggered isomer rather than 5.47 kcal/mol above as is the case when d functions are added to the standard LanL2DZ basis set.

All evidence indicates the difficulty of describing high-valence systems without using d functions in the basis set. It is the set of ten ring-to-ring bonds of the staggered isomer that are most affected and the set of five ring-to-ring bonds of the eclipsed isomer that are least affected by the presence of d functions. It is the eclipsed isomer in which only two Al atoms have five bonds while the rest have only four, which is favored when d functions are not present and the staggered isomer in which all 12 aluminum atoms form five bonds each which is energetically favored when d functions are added to the basis set.

Due to the fact that the LanL2DZ basis set is incapable of describing high-valency situations without the addition of d functions, all geometry and frequency determinations of the $Al@Al_{12}$ cluster were completed using the LanL2DZ(d) basis set.

IV. THE $Al@Al_{12}^{-}$ ANIONIC STATIONARY POINTS

The Al_{77} cluster of Ecker *et al.* [1] has a core of one aluminum atom surrounded by a cage of 12 atoms (that enclosed by two more cage layers of 44 and 20 atoms, respectively). They report an average oxidation number of +0.23. However, it is clear that variation between layers is probable and it is not immediately apparent what charge should be contained by the inner 13 Al atoms that we investigate here. Numerous sorties examining the cation, neutral, and anion of the $Al@Al_{12}$ cluster were made. No atom-in-a-cage structure was found for the cation, while one such structure of C_1 symmetry was located on the doublet neutral surface. It was the anionic cluster that provided the most highly symmetric potential-energy surface. Thus, first we report our findings for the $Al@Al_{12}^{-}$ anionic cluster.

A. The $Al@Al_{12}^{-}$ staggered isomer

The $Al@Al_{12}^{-}$ anionic cluster depicted in Fig. 1 is found to have a staggered geometrical structure with icosahedral symmetry and a quadruply degenerate G_u HOMO at the B3LYP/LanL2DZ(d) level of theory. Thus there are only two types of atoms in this structure and two types of bonds. The central atom interacts with each of the surface atoms equally and is 2.679 Å distant from each. The surface bonds are each 2.817 Å long. This is a slight expansion from the Al_{12} D_{5d} staggered isomer in which the average bond length was 2.760 Å. However, it should be remembered that the longest bonds of the Al_{12} cluster were the ring-to-ring bonds, which did have a bond length of 2.847 Å, slightly longer than each of the surface bonds in the $Al@Al_{12}^{-}$ anionic cluster.

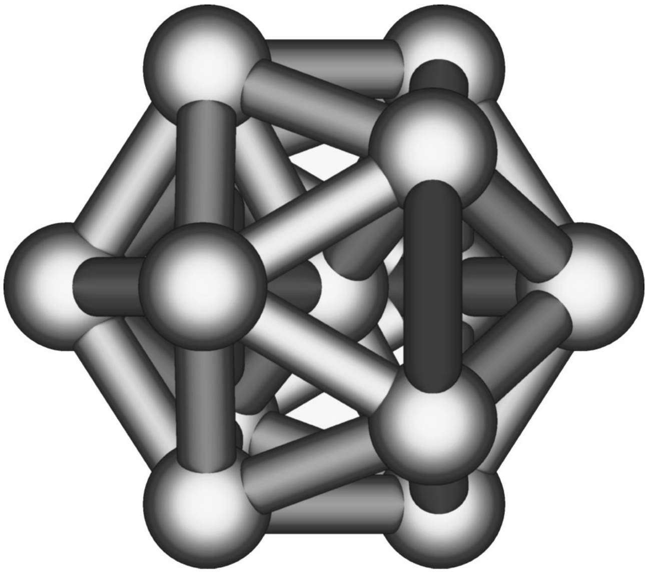

FIG. 1. The $Al@Al_{12}^{-}$ icosahedral minimum.

Ecker *et al.* reported a distorted icosahedron structure for the central $Al@Al_{12}$ part of their Al_{77} cluster with a rather large variation in center-to-surface bond lengths (2.675–2.868 Å) and surface bonds as short as 2.640 Å. Their average center-to-surface bond length of 2.760 Å is not very different from our prediction of 2.679 Å, but the differences between their observations and our predictions make for a rather strong argument that the core thirteen atoms of their Al_{77} cluster is not an anionic moiety.

The harmonic vibrational frequency analysis at the B3LYP/LanL2DZ(d) level of theory did confirm this icosahedral structure as a minimum on the potential-energy surface. Lower symmetry isomers were used as starting points, but optimization always led to this structure. The harmonic vibrational frequencies of this minimum on the B3LYP/LanL2DZ(d) potential-energy surface range from 46 to 355 cm^{-1}. The lowest of these frequencies correspond to distortions of the surface atoms, while the highest correspond to asymmetrical movements of the central Al atom. The ‘‘breathing’’ mode is located at 217 cm^{-1}.

Another point of interest is the location of charge within this cluster computed at the B3LYP/6-311(2df) level of theory. In this cluster, the difference between the Mulliken charges and the natural charges of the NBO analysis are great. According to the Mulliken charges, the central atom supports a charge of $+1.915e^{-}$, while the natural charge of that atom according to the NBO analysis is $-0.937e^{-}$. This difference could arise from the geometrical nature of the Mulliken analysis ‘‘bleeding’’ the central Al atom of its electrons, whereas the NBO analysis reports that the central atom is highly involved in the bonding scheme of the cluster. The NBO analysis reports high occupancy of the $3s$ and $3p$ orbitals of the central atom, listing them frequently in the second-order interactions as making highly energetic contributions to the stabilization of the molecule, e.g., a donation from one of those p orbitals to an orbital that is antibonding for two Al atoms on opposite sides of the cluster which stabilizes the molecule by 930 kcal/mol. It is the high occupancy of these valence orbitals of the central atom in the NBO analysis that results in the natural charge of $-0.937e^{-}$.

The energy of encagement for the central aluminum anion, i.e., $E(Al@Al_{12}^{-})-E(Al_{12})-E(Al^{-})$ is 151 kcal/

TABLE I. Geometrical parameters for the various Al_{12} and $\mathrm{Al@Al}_{12}$ stationary points optimized at the B3LYP/Lan2LDZ(d) level of theory. Bond lengths are in angstroms.

Cluster	Peak-to-ring	Ring	Ring-to-ring	Center-to-peak	Center-to-ring
Al_{12} (staggered)	2.743	2.681	2.847		
Al_{12} (eclipsed)	2.713	2.696	2.671		
$\mathrm{Al}_{13}{}^{-}$ (staggered)	2.817	[a]	[a]	2.817	[a]
$\mathrm{Al}_{13}{}^{-}$ (eclipsed)	2.778	2.829	2.623	2.698	2.742
Al_{13} (C_1)		2.606 to 3.147		2.635 to 2.850 avg. 2.744	
Al_{13} (expt.)[b]		2.640 to 3.140		2.675 to 2.868 avg. 2.760	

[a] Symmetry related to others in that group.

[b] Reference [1].

mol at the B3LYP/6-311+(2df)//B3LYP/LanL2DZ(d) +ΔZPVE level of theory. Diffuse functions were added to the basis for this calculation in order to give a reasonable description of the aluminum anion [the B3LYP/6-311+(2df) level of theory gives an electron affinity of 8.8 kcal/mol compared to the experimental value of 10 kcal/mol [18]]. This large stabilization implies that the $\mathrm{Al@Al}_{12}{}^{-}$ anionic cluster should be quite stable and suggests the interesting possibility of the synthesis of a compound similar to that of Hiller *et al.* [2], but with an additional aluminum atom in the center of the Al_{12} cage. That central atom could, as Ecker *et al.* [1] pointed out, be considered metallic as is the case in the Al_{77} cluster.

B. The $\mathrm{Al@Al}_{12}{}^{-}$ eclipsed stationary point

The $\mathrm{Al@Al}_{12}{}^{-}$ eclipsed isomer, like the related Al_{12} eclipsed stationary point, has D_{5h} symmetry and each ring atom bound to only one atom in the other ring. Here the two peak atoms are actually closer to the center atom (2.698 Å) than are the ten ring atoms (2.742 Å). The peak-to-ring bond lengths are 2.778 Å and the ring bonds measure 2.829, 0.065, and 0.133 Å longer than their equivalents in the vacant-center cluster. The ring-to-ring bonds, on the other hand, are even shorter than those found in the Al_{12} stationary point. At 2.623 Å, they are the shortest Al-Al bonds found in this study. Also, we note that the average center-to-surface bond has increased by 0.056 Å and the average of the surface bond lengths is only 0.007 Å longer than the length of the surface bonds in the eclipsed minimum.

Unlike the eclipsed isomer of the Al_{12} cluster, this stationary point is shown by the harmonic vibrational frequency analysis to be a true transition state. There is one imaginary frequency and it corresponds to ring-ring rotation, leading directly to the staggered minimum. Thus, this stationary point could be considered as a transition state for pseudorotation or mixing of the surface atoms (remembering that in the minimum the icosahedral symmetry permits the equivalent designation of any set of rings).

The location of charge in this transition state is quite similar to that in the minimum. The NBO analysis reports a slightly larger negative charge on the central atom in this eclipsed conformation ($-1.057e^{-}$) and also a very slight negative charge on the two peak atoms ($-0.011e^{-}$).

Energetically, the transition state for pseudorotation lies only 2.92 kcal/mol above the staggered minimum at the B3LYP/LanL2DZ(d)+ΔZPVE level of theory. As was the case for the Al_{12} cluster, the expansion of the basis set makes little difference in this separation, again incrementing the faith in the reliability of the LanL2DZ(d) results. At the B3LYP/6-311(2df)//B3LYP/LanL2DZ(d)+ΔZPVE level of theory, the difference is predicted to be 3.86 kcal/mol. Hence, interconversion between two equivalent staggered minima should be facile and our calculations predict this cluster to be a rather fluxional species.

V. THE NEUTRAL $\mathrm{Al@Al}_{12}$ CLUSTER

As mentioned earlier, the neutral and cationic $\mathrm{Al@Al}_{12}$ clusters were also studied. On the cationic surface, no minima with an atom-in-a-cage structure were found. The cation lacks sufficient electrons for bond formation, all optimization processes leading to complete changes of the cluster away from hypervalency. The neutral, too, shows the effects of losing bonding electrons, with some of the distances between surface atoms becoming very long. One minimum was located on the neutral potential-energy surface. However, with the loss of one electron from the formerly fully occupied quadruply degenerate G_u HOMO, the cluster has also lost all symmetry; the minimum has only C_1 symmetry.

This neutral structure does maintain the atom-in-a-cage structure and is remarkably similar to the core of the Al_{77} cluster of Ecker *et al.* [1] as can be seen in Table I. They report center-to-surface bond lengths ranging from 2.675 to 2.868 Å with an average length of 2.760 Å. The equilibrium geometry of the neutral $\mathrm{Al@Al}_{12}$ cluster predicted at the B3LYP/LanL2DZ(d) level of theory has center-to-surface bond lengths that range from 2.635 to 2.850 Å and averaging 2.744 Å. Here we see that the predictions agree very well with the core of the experimental cluster, with only slight differences to the side of shorter bond lengths, but it must be remembered that the $\mathrm{Al@Al}_{12}$ core in the experimental molecule is surrounded by additional layers that could easily lengthen the central bonds.

Also we note that the measured ESR spectrum indicated that the Al_{77} species was paramagnetic with $S \geqslant \frac{1}{2}$. It is reasonable that the spin could be located in the core 13 atoms. This neutral cluster is a doublet with the spin density spread throughout rather than being centered on any one atom (e.g., the center atom) according to the Mulliken spin densities. Again, our predictions are in agreement with the observations of Ecker *et al.* [1].

The harmonic vibrational frequency analysis does characterize this stationary point as a minimum of the potential energy surface. All frequencies are positive. However, the lowest harmonic vibrational frequency is located at 9 cm^{-1}. This vibration and other low-frequency vibrations correspond to cage distortion motions. The ''breathing'' vibration has a frequency of 260 cm^{-1} and three of the four highest-frequency vibrations (327, 336, and 352 cm^{-1}) correspond to movement of the central atom within the cage. In comparison to the same modes for the anionic $Al@Al_{12}^{-}$ minimum, the lowest frequency is clearly lower, the movement of the central atom within the cage is also slightly lower, but the ''breathing'' frequency is 43 cm^{-1} higher.

According to the Mulliken charges calculated using the 6-311(2df) basis set, the central atom supports a large positive charge in this neutral species. This was also the case in the anionic cluster and we believe this to be due to weaknesses in the algorithm. The NBO analysis computed with the same basis set paints a completely different picture. Again similar to the anionic cluster, the central atom is reported to have a large negative charge ($-1.292e^{-}$) and this is due to its large participation of its atomic orbitals in the bonding scheme of the cluster.

The energy of encagement for the neutral $Al@Al_{12}$ cluster is significantly less than that of the anion. Still, the value of 86.8 kcal/mol calculated at the B3LYP/6-311+(2df)//B3LYP/LanL2DZ(d) level of theory shows that encagement is a very exothermic reaction.

The difference in the encagement energies for the neutral and anionic $Al@Al_{12}$ clusters also reflects another very interesting point. The electron affinity of the $Al@Al_{12}$ cluster is predicted to be an astonishingly high 73.9 kcal/mol (the EA of the Al atom calculated at the same level of theory is only 8.8 kcal/mol). This high electron affinity is due to the fact that one extra electron fills up the HOMO of the anion, a quadruply degenerate G_u orbital. Without that electron, the cluster could be considered electron deficient, lacking sufficient electrons to fully form all the surface bonds. Considering the stabilization offered by adding an electron to the neutral $Al@Al_{12}$ cluster, we suggest that using electron donor groups as substituents should help facilitate the synthesis of this atom-in-a-cage structure.

VI. CONCLUSIONS

The potential-energy surfaces of Al_{12} and $Al@Al_{12}^{+/0/-}$ have been searched extensively at the B3LYP/LanL2DZ(d) level of theory. The addition of *d* functions to the LanL2DZ basis set was seen to be essential, as they drastically changed both relative energies and surface shapes. The located stationary points were then investigated more rigorously through the use of all-electron basis sets as large as 6-311+(2df).

Two stationary points were located for the Al_{12} cluster. A distorted icosahedral structure of D_{5d} symmetry is the global minimum and a structure with eclipsed rings and D_{5h} symmetry was found to be a saddle point of Hessian order three lying 6.88 kcal/mol above the minimum.

No atom-in-a-cage structures were found for the cationic Al_{13}^{+} cluster. Two stationary points were found on the anionic $Al@Al_{12}^{-}$ B3LYP/LanL2DZ(d) potential energy surface. These were quite similar to the Al_{12} stationary points except that the staggered minimum had icosahedral symmetry and the D_{5h} eclipsed structure was a true transition state for pseudorotation or mixing of surface atoms. That transition state lies only 3.86 kcal/mol above the minimum at the B3LYP/6-311(2df)//B3LYP/LanL2DZ(d)+ΔZPVE level of theory.

Only one stationary point was located for the doublet neutral $Al@Al_{12}$ cluster. This minimum of C_1 symmetry is in remarkable agreement geometrically with the core of the Al_{77} cluster of Ecker *et al* [1]. Taking the average of the absolute difference between their reported minimum, maximum, and average center-to-surface bond lengths and our predicted values for those parameters yields an extremely satisfying 0.025 Å. Also, the experimental work showed the Al_{77} cluster to be paramagnetic with $S \geqslant \frac{1}{2}$, which agrees with our doublet prediction.

The energy of encagement of the central aluminum anion in both the case of the anion and neutral $Al@Al_{12}$ is quite large and indicates that the encagement process would be quite exothermic. In the case of the anion that energy is 151 kcal/mol and for the neutral is 86.8 kcal/mol, the difference reflecting the large electron affinity of the $Al@Al_{12}$ cluster, 73.9 kcal/mol. We hope that these predictions will instigate further experimental investigation into these intriguing clusters.

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