

Al\(_{12}\)Cu Superatom as Stable Building Block of Ionic Salts

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Supporting Information

ABSTRACT: The neutral copper aluminum cluster complex Al\(_{12}\)CuM\(_3\) \(\{M = \text{K, K}_2\text{O, and K(2,2,2-crypt)}\}\) has been investigated at the PBE96 level of theory. It is found that Al\(_{12}\)Cu could be considered a superatom mimic of a phosphorus atom. It shows large electron affinity and is able to receive three electrons from elements or compounds with low ionization energies like K, K\(_2\)O, or K(2,2,2-crypt) to become a stable electronic closed shell with a large gap between the highest occupied and lowest unoccupied molecular orbitals (HOMO-LUMO gap). Theoretical calculations confirm that similar to the phosphorus atom in PK\(_2\), the superatom Al\(_{12}\)Cu cluster could form ionic salts, as shown from stable dimers, trimers, and tetramers of the Al\(_{12}\)Cu\{K(2,2,2-crypt)\} complex. On the basis of the maintenance of its integrity in these assemblies it could be predicted that Al\(_{12}\)CuM\(_3\) holds great potential as a building block for the development of future nanostructured materials. Furthermore, the choice of the K(2,2,2-crypt) molecules to stabilize the salt opens a route to experimentally generate cluster base ionic salts, and we expect that our work motivates experimental investigations of these assemblies.

1. INTRODUCTION

The search for stable clusters is one of the most active fields in experimental and theoretical materials science today aimed to develop nanostructured materials with tailored properties.\(^1\)-\(^8\) It has been found that collective phenomena exhibited in bulk materials break down for very small sizes. For example, small clusters of Rh, a nonmagnetic material, are magnetic,\(^7\) noble elements like gold, with a high electron affinity, and platinum have shown to act as a catalyst on the nanoscale.\(^10,11\) It was found that for very reactive elements like gold and platinum turn active catalysts when under small sizes. For example, small clusters of Rh and Pt have shown to act as a catalyst on the nanoscale.\(^10,11\) It was found that for very reactive elements like gold and platinum turn active catalysts when under small sizes.

Furthermore, experiments on the dissociation of clusters showed that the stable sizes were the favored fragmentation products and that more energy was required to fragment these sizes.\(^14,15\)

In simple metals, a confined free electron (CFE) model is a good representation of the electronic spectrum, and Knight and Ekardt\(^12,16\) proposed such a model to explain the experimentally observed stability of the alkali clusters. In this model, the nuclei with the innermost electrons form a positively charged background that acts over the valence electrons of the system, resulting in the arrangement of the cluster’s valence electrons into 1S\(^2\), 1P\(^6\), 1D\(^{10}\), 2S\(^2\), 1F\(^{14}\), 2P\(^{6}\), ... subshells similarly to the 1s\(^2\), 2s\(^2\), 2p\(^6\), ... subshells found in individual atoms. Because each alkali atom contributes with one electron to the valence pool, the stable sizes at 2, 8, 18, 20, 40... all correspond to electron counts that result in filled electronic shells. At larger cluster sizes the extended cluster orbitals tend to condense into highly degenerated shells and geometrical effects begin to contribute to the stability.\(^17\)-\(^19\) For example, experiments on sodium clusters containing up to several hundred atoms showed that the principal peaks in the mass spectrum could be reconciled as being due to geometric effects.\(^17\)

These principles that rule electronic and geometrical stability have been successfully applied to other metallic clusters. Experimental observations by Castleman and coworkers\(^1\) on...
the reactivity of aluminum cluster anions with oxygen found that while most clusters were etched away by oxygen, clusters containing 13 and 23 atoms were relatively intact. Subsequent theoretical studies by Khanna and Jena, and Gong and Kumar showed that both Al_{13}^- and Al_{23}^- clusters correspond to closed-shell systems. For example, Al_{13}^- is a stable chemical cluster that would neither give nor receive electrons as it has a large HOMO–LUMO gap of 1.87 eV. The cluster also showed to be energetically stable as it would take almost 4.65 eV to remove an Al atom from Al_{13}^− as opposed to 3.02 and 2.08 eV required to remove an atom from Al_{12}^− and Al_{14}^−, respectively. Furthermore, the electronic structure of Al_{13}^- showed 40 valence electrons (three valence electrons per Al atom) that can be arranged according to the CFE model in an 1S^2, 1P^6, 1D^10, 2S^2, 1F^14, and 2P^6 closed-shell configuration. Subsequent theoretical and experimental studies indicated that Al_{13} has a large electron affinity of 3.57 eV, and having 39 valence electrons is only one electron short of a 40 electron closed shell. 

Over the past few years, superatoms resembling alkaline earth, multiple valence, superalkali, transition metals, Over the past few years, superatoms resembling alkaline earth, multiple valence, superalkali, transition metals, superatomic assemblies. Both Reber et al. and Qiong found local minima resulting from a unique orientation of the cationic and anionic units in their cluster assemblies. In experiments, however, it is likely that random orientations of the clusters will favor configurations in which the metal–metal intermolecular interactions will collapse the building units toward the more stable global minimum.

The aim of this paper is to explore if truly stable ionic superatomic assemblies are indeed possible. Motivated by the work of Kumar and Yoshiyuki that reported a high-spin icosahedral ground state for Al_{12}Cu with a magnetic moment of 3 μ_B, we investigate if Al_{12}Cu, being able to accept three electrons from elements and compounds with a low ionization energy to form (Al_{12}Cu)^5−(M')₃ species, may be a suitable candidate to form stable nanostructures. In particular, the following questions are addressed: Is the large negative charge in the anionic (Al_{12}Cu)^5−superatom able to overcome the intermolecular attractions in the ionic salts preserving its identity? How large should an ideal cationic M species needs to be to help sustaining the assembly through steric hindrance?

Our study shows that neither K nor K_3O cations can avoid collapse of the ionic species in the cluster assemblies and that it is only the bulkier K(Krypt-222) cation that allows the formation of chemically and energetically stable ionic salts [Al_{12}Cu(K(krypt-222))]₃n (n = 1–4) of the Al_{12}Cu cluster superatom in a similar way as phosphorus does in PK₃.

2. COMPUTATIONAL METHOD

The theoretical calculations are carried out within the density functional formalism with the description of exchange-correlation effects at the generalized gradient approximation level by means of the Perdew, Burke, and Ernzerhof (PBE96) functional. The electronic orbitals and eigenstates are determined by using a linear combination of Gaussian atomic-type orbital molecular orbital (LCGTO) approach in the deMon2k software. The calculation of four-center electron repulsion integrals is avoided using a variational fitting of the Coulomb potential, and the exchange correlation energy and potential are calculated via a numerical integration of the fitted density using the GEN-A2 auxiliary function set. All electrons of the Al, Cu, K, and O atoms are treated explicitly using the double-ζ valence plus polarization (DZVP) basis sets. Relativistic effective core potentials with 1, 4, 5, 6, 3, and 19 valence electrons for K, C, N, O, Al, and Cu were employed, respectively, with their corresponding basis sets to speed up the calculations of the larger [Al_{12}Cu(K(krypt-222))]₃n (n = 1–4) systems, which range from 202 to 808 atoms. The geometry optimization used a quasi-Newton method in internal delocalized coordinates and all possible spin configurations were investigated to determine the most stable states. Partial charges were determined using a natural bond orbital (NBO) analysis.

To further eliminate any uncertainty associated with the choice of basis set, the numerical procedure, and the use of pseudo potentials, we carried out supplementary all-electron calculations using the Naval Research Laboratory Molecular Orbital Library (NRLMOL) set of codes developed by Pederson and coworkers. For these calculations the same PBE96-generalized gradient approximation used in deMon2k was employed. We found excellent agreement in the optimized geometries and energy order of the investigated spin states for the clusters between deMon2k and NRLMOL calculations.
3. RESULTS AND DISCUSSION

3.1. Al\textsubscript{12}Cu Superatom. As previously noted, several studies have explored Al superatoms as potential building blocks of ionic materials, but strong intermolecular interactions between these have limited the potential to build truly stable cluster assemblies. In this work we study the Al\textsubscript{12}Cu neutral species with a goal to design a stable superatom with a large negative charge because such a system can result in ionic compounds with increased stability. Kumar and Kawazoe reported the finding of a high-spin icosahedral ground state for Al\textsubscript{12}Cu with a magnetic moment of 3\(\mu\)B in accordance with the Hund’s rule of maximum spin at half-filling of a P shell forming an open-shell superatom.\textsuperscript{42} Several possible geometries and spin states were investigated in our study, and it was found that the most stable structure for Al\textsubscript{12}Cu did correspond to the Cu atom inside a slightly distorted icosahedral cage with \(D_3d\) symmetry and Al–Al and Al–Cu bonds of 2.79 and 2.65 Å, respectively, as shown in Figure 1, and presenting a quartet spin state (having three unpaired electrons), in agreement with the previous report.\textsuperscript{42} An analysis of the electronic structure of Al\textsubscript{12}Cu accounts for a total of 37 delocalized valence electrons (three electrons for each Al and one electron for the Cu atom) arranged in \(1S^2, 1P^6, 1D^{10}, 2S^2, 1F^{14}\), and \(2P^3\) subshells according to the CFE model, as shown by the one-electron energy levels and molecular orbital isosurfaces in Figure 2. Note that the filled 3d states of Cu are located between the 1P\textsuperscript{6} and 1D\textsuperscript{10} states. Notably, the highest occupied energy levels correspond to triple-degenerate 2P\textsuperscript{3} states three electrons short to complete the shell, similar to a phosphorus atom with a [Ne] 4s\textsuperscript{2}3p\textsuperscript{3} configuration. Moreover, our calculated electron affinity of 2.92 eV, in good agreement with the experimental value of 3.24 ± 0.03 eV reported by Pal et al.,\textsuperscript{57} indicated a larger tendency of Al\textsubscript{12}Cu to receive electrons. Pal et al. also employed a Basin-hopping global optimization method and found a slightly distorted icosahedral with \(D_3d\) symmetry to be ground-state geometry of the anionic Al\textsubscript{12}Cu\textsuperscript{−}. The gas-phase anionic Al\textsubscript{12}Cu\textsuperscript{−} has also been produced as reported in an experimental and theoretical study by Roach et al.\textsuperscript{58} The authors, however, noted that the cluster was oxygen-etched and did not show signs of chemical stability, presenting a small HOMO–LUMO gap of only 0.2 eV. The rationale for this behavior is rooted in its electronic structure. One extra electron is not enough to complete the cluster’s 2P subshell to generate a stable species. The 2P subshell of Al\textsubscript{12}Cu cluster can, however, be completed by the addition of three electrons, as discussed later.

3.2. Al\textsubscript{12}CuK\textsubscript{n} Clusters and Its Assemblies. With the goal to obtain a closed-shell cluster, we studied the interaction of K atoms (an electron donor with low ionization energy) with the Al\textsubscript{12}Cu cluster. We investigated the charge transfer by calculating NBO charges and the energy gained with successive
additions of K atoms to Al$_{12}$Cu, incremental binding energy (IBE), in Al$_{12}$CuK$_n$ by using the equation

$$\text{IBE} = E[\text{Al}_1\text{CuK}_n] - E[K] - E[\text{Al}_1\text{CuK}_{n-1}],$$

with $n = 1-5$.

Here $E[X]$ represents the total energy of the gas-phase species. Note that according to this definition a positive IBE corresponds to a bound structure and a larger value of IBE is indicative of an energetically more stable structure. Addition of one K atom resulted in a large energy gain of 2.0 eV to form Al$_{12}$CuK in which the K sits on top of a hole of a slightly distorted Al$_{12}$Cu cage (Figure 1). The one-electron energy levels indicate that one electron was transferred to the 2P subshell of Al$_{12}$CuK that now presents a triplet state with two still unpaired electrons and a small HOMO–LUMO gap (and thus in the chemical stability of the Al$_{12}$CuK$_3$ species that showed large energy gains for the second and third K atoms of 1.93 and 1.85 eV, respectively, and a drop in the IBE after 3 K atoms to only ~0.7 eV (Figure 4a). The optimized geometries and electronic charges for these species are presented in Figure 1. Moreover, the calculations also indicate a progressive increase in the HOMO–LUMO gap (and thus in the chemical stability) with each addition of K atoms as the 2P subshell gets filled with the charge given by the K atoms, reaching a maximum gap of 1.4 eV for the compact closed-shell Al$_{12}$CuK$_3$ cluster (Figures 1 and 3). We confirm the ionic nature of this species via our population analysis that found ~2.88 and 0.96 electronic charges in Al$_{12}$Cu and each K atom, respectively.

Figure 2. One-electron energy levels and molecular orbital isosurfaces for Al$_{12}$Cu. The main and angular quantum numbers for the delocalized superorbitals and the 3d Cu localized orbitals are also given. The 2P superorbitals are marked in a blue rectangle. Solid black lines and dotted red lines represent, respectively, occupied and unoccupied states.

Our next step in the investigation of ionic cluster assemblies was to study the structural and electronic properties of dimers of the ionic Al$_{12}$CuK$_3$ cluster. Several initial orientations of the (Al$_{12}$CuK$_3$)–(Al$_{12}$CuK$_3$) dimer were prepared and full-geometry optimizations were performed. The initial geometries showed signs of structural stability, and we did actually find a stable dimer in which the Al$_{12}$CuK$_3$ units remain separated and exhibit a large HOMO–LUMO gap of 1.36 eV, as shown in Figure 5a. However, because of the metal–metal interactions between the Al$_{12}$Cu units, another more stable complex was also found with an Al–Al bonding between adjacent cores at a short distance of 2.90 Å. This structure resulted in being more stable by 1.21 eV and had a smaller HOMO–LUMO gap of only 0.64 eV, which is indicative of less chemical stability (Figure 5a). This result is also consistent with a report by Ashman et al. who studied the mobility of alkali atoms on the Al$_{13}$ surface. The authors found that the barrier for the motion of a K atom from one hollow site to another is <0.13 eV, indicating that it may be possible for K atoms to be mobile at ordinary temperatures and hence are not good protecting cations for the aluminum core.

3.3. Al$_{12}$Cu(K$_3$O)$_n$ Clusters and Its Assemblies. We then changed our strategy by turning efforts to the use of molecular counterions rather than atomic ions. These ions have two main advantages. First, they present low ionization energies like single alkali atoms assuring a good charge transfer when forming a molecular salt. Second, and the more important advantage, is that the bulkier nature of these molecular counterions increases the steric hindrance, which helps in avoiding the agglomeration of separate clusters into a bulk material.

Motivated by the work of Reber et al. who reported Al$_{12}$M$_2$O as a strongly bound molecule that retains its integrity in ionic complexes of the type (Al$_{12}$M$_2$O)$_n$ (M = Na and K, n = 1–5) with separated Al$_{13}$ and M$_2$O units; we first studied the binding of the super alkali K$_3$O molecule with our Al$_{12}$Cu superatom aimed to form a stable closed-shell species like the one found for Al$_{12}$CuK$_3$. We begin by investigating the charge transfer and the energy gained with successive additions of K$_3$O.
Al\textsubscript{12}Cu, which is in need of three electrons to complete its 2P subshell as previously mentioned. The analysis of the electronic energies (IBEs) for the (a) Al\textsubscript{12}Cu\textsubscript{(K\textsubscript{3}O)}\textsubscript{n} and (c) Al\textsubscript{12}Cu\textsubscript{(Crypt)}\textsubscript{n}, n = 1–5 clusters [K. Zhang et al., J. Phys. Chem. C 2015, 119, 5129–5137, DOI: 10.1021/jp512261v].

molecules (IBE) in forming Al\textsubscript{12}Cu\textsubscript{(K\textsubscript{3}O)}\textsubscript{n} by using the equation

\[ \text{IBE} = E[\text{Al}_{12}\text{Cu}(\text{K}\textsubscript{3}O)_{n}] - E[\text{K}\textsubscript{3}O] - E[\text{Al}_{12}\text{Cu}(\text{K}\textsubscript{3}O)_{n-1}], \]

with \( n = 1–5 \)

The addition of the first K\textsubscript{3}O resulted in a large energy gain of 6.19 eV to form Al\textsubscript{12}Cu\textsubscript{K\textsubscript{3}O} in which the O atom strongly binds to an Al atom at a short distance of 1.77 Å. This distance is within the range of 1.7 to 2.0 Å reported for the Al–O bond in Al\textsubscript{12}O\textsubscript{2} (\( n = 1–5 \)) clusters by Sun et al.\textsuperscript{39} Surprisingly, Al\textsubscript{12}Cu\textsubscript{K\textsubscript{3}O} presented a closed-shell configuration (Figure 1) with a HOMO–LUMO gap of 0.7 eV. This result is intriguing given that according to our population analysis only 1.43 electrons are transferred from the K\textsubscript{3}O superalkali cluster into Al\textsubscript{12}Cu, which is in need of three electrons to complete its 2P subshell as previously mentioned. The analysis of the electronic structure sheds light onto this apparent contradiction. According to the one-electron energy levels shown in Figure 6a, a set of occupied energy levels of K\textsubscript{3}O lies above the unoccupied 2P levels of Al\textsubscript{12}Cu. The bonding combinations of these levels give rise to an Al\textsubscript{12}CuK\textsubscript{3}O complex that exhibits a polar covalent interaction between the two units. The polar nature of the bonding is attested by the calculated charge transfer and the covalent character is attested by the observed bonding between Al and O. Furthermore, the stronger interaction in this case becomes evident from the large energy gain of 6.16 eV for the addition of K\textsubscript{3}O to Al\textsubscript{12}Cu. This energy is three times larger than the energy gain (1.99 eV) for the addition of a single K to Al\textsubscript{13}Cu. The addition of another K\textsubscript{3}O to Al\textsubscript{13}Cu\textsubscript{K\textsubscript{3}O} also resulted in a large energy gain of 4.61 eV. The population analysis of the optimized Al\textsubscript{12}Cu\textsubscript{(K\textsubscript{3}O)}\textsubscript{3} cluster indicates an increase in the charge transfer toward the Al\textsubscript{12}Cu core, which now acquires a negative ~2.49 electronic charge (Figure 1). The energy levels for this cluster reveal a 2P\textsuperscript{5} configuration for the highest occupied subshell in a doublet state with still one unpaired electron and a smaller HOMO–LUMO gap of 0.33 eV. Finally, the addition of a third K\textsubscript{3}O resulted in an energy gain of 4.46 eV accompanied by additional charge transfer such that the Al\textsubscript{12}Cu core now acquires a negative ~3.38 charge in the closed-shell Al\textsubscript{12}Cu\textsubscript{(K\textsubscript{3}O)}\textsubscript{3} species with a HOMO–LUMO gap of 0.67 eV. Further addition of K\textsubscript{3}O resulted in smaller energy gains and species with smaller HOMO–LUMO gaps, as shown in Figure 4b. These results suggested that the stable closed-shell Al\textsubscript{12}Cu\textsubscript{(K\textsubscript{3}O)}\textsubscript{3} cluster can be a promising candidate as a building block of ionic assemblies. To explore this we prepared several initial orientations of the Al\textsubscript{12}Cu\textsubscript{(K\textsubscript{3}O)}\textsubscript{3}–Al\textsubscript{12}Cu\textsubscript{(K\textsubscript{3}O)}\textsubscript{3} dimer, which were then fully optimized. Notably, we again found the formation of a stable complex with separated Al\textsubscript{12}Cu\textsubscript{(K\textsubscript{3}O)}\textsubscript{3} units exhibiting a HOMO–LUMO gap of only 0.47 eV, as shown in Figure 5b. However, as in the case of the (Al\textsubscript{12}Cu\textsubscript{K\textsubscript{3}O})\textsubscript{2} and (Al\textsubscript{12}Cu\textsubscript{K\textsubscript{3}O})\textsubscript{3} dimers, strong metal–metal interactions between the Al\textsubscript{12}Cu units conducted to another more stable complex with the presence of Al–Al bonding between adjacent cores at a distance of 2.69 Å. This structure resulted in being more stable by 0.76 eV and had a smaller HOMO–LUMO gap of only 0.15 eV in a triplet-state configuration (Figure 5b).

Interestingly, our results disagree with the report of Reber et al.,\textsuperscript{41} wherein the lowest energy dimer of (K\textsubscript{3}OAl\textsubscript{13})\textsubscript{2} was found to be a bent structure with oxygen occupying on-top positions at the Al\textsubscript{13} surface and with an energy barrier of ~0.14 eV toward the formation of the Al\textsubscript{15}–K\textsubscript{3}O\textsubscript{5} species. To investigate the cause of discrepancy, we also calculated the Al\textsubscript{13}K\textsubscript{3}O–Al\textsubscript{13}K\textsubscript{3}O dimers starting from several initial configurations and found that it is only when the species are disposed such that the K\textsubscript{3}O on one Al\textsubscript{13}K\textsubscript{3}O is oriented toward the Al\textsubscript{13} side of the second Al\textsubscript{13}K\textsubscript{3}O that we are able to reproduce the results of ref. 41. All other possible configurations of the dimers led to the formation of more stable Al\textsubscript{15}–K\textsubscript{3}O\textsubscript{5} species without any energy barrier. In actual experiments, it is likely that random orientations of the clusters will favor configurations in which the metal–metal intermolecular interactions will collapse the building units toward the more stable global minimum with the loss of the individual cluster identities and properties.

Similarly, another study by Qiong et al.\textsuperscript{51} showed that the halogen superatom Al\textsubscript{13}C maintains its integrity in ionic complexes when bonding with K atoms in the form [(Al\textsubscript{13}C)(KCaAl\textsubscript{13})\textsubscript{n}] (\( n = 1–5 \)). We again calculated these clusters and found that it is only in the structural configuration given by the author that the species retains its identity and that other possibilities resulted in collapsing of the aluminum clusters into more stable

Figure 4. HOMO–LUMO gap (HL gap) and incremental binding energies (IBEs) for the (a) Al\textsubscript{12}Cu\textsubscript{(K\textsubscript{3}O)}\textsubscript{n}, (b) Al\textsubscript{12}Cu\textsubscript{(K\textsubscript{3}O)}\textsubscript{n} and (c) Al\textsubscript{12}Cu\textsubscript{(Crypt)}\textsubscript{n}, n = 1–5 clusters.
conifigurations. These results suggest that an even larger molecular cation is needed to prohibit fusion of aluminum clusters in the formation of ionic solids.

3.4. Al_{12}Cu(Crypt)_n Clusters and Their Assemblies. The results in previous sections indicate that the K and K_3O ions cannot prevent coalescence of the Al_{12}CuM_3 (M = K and K_3O) cluster due to their smaller sizes and we therefore choose the bulkier K encapsulated K(2.2.2-cryptand), from now on called Crypt, as the electron donor for our Al_{12}Cu superatom with the hope that its larger size could stabilize the ionic assemblies. Cryptands are a family of synthetic bi- and polycyclic multidentate ligands for a variety of cations. These molecules are 3D analogues of crown ethers but are more selective, complex the guest ions more strongly, and exhibit low ionization energies. We begin by studying the binding of the Crypt molecules with our Al_{12}Cu superatom with a goal to obtain a stable closed species like the ones found for Al_{12}CuK_3 and Al_{12}Cu(K_3O)_3. We investigated the charge transfer and the energy gained with successive additions of Crypt molecules (IBE) in forming Al_{12}Cu(Crypt)_n in a similar way as we did above for the K and K_3O electron donors.

The addition of the first Crypt resulted in a large energy gain of 3.19 eV to form the Al_{12}CuCrypt complex in which the K atom of the Crypt sits on top of an Al atom of the Al_{12}Cu cage at a distance of 4.56 Å (Figure 1). The optimized Al_{12}CuCrypt has multiplicity of 3 and a small HOMO–LUMO gap of 0.14 eV. The state with spin multiplicity of 1 is energetically degenerate with this state. Figure 6b presents the one-electron energy levels for Al_{12}Cu, Crypt, and Al_{12}Cu(Crypt)_n, n = 1–3. It can be seen that a single occupied energy level from the Crypt lies above the 2P unoccupied states of Al_{12}Cu and that it is this Crypt state that transfers one electron to form a 2P^1 configuration in the triplet state of Al_{12}CuCrypt. The population analysis results are consistent with this observation and show 1.04 and −1.04 electronic charges for the Crypt and Al_{12}Cu fragments, respectively. The calculated energy gain of 3.19 eV for the addition of Crypt to Al_{12}Cu is >1 eV larger than the energy gain for the addition of a single K atom to Al_{12}Cu of only 1.99 eV.

The addition of second Crypt to Al_{12}Cu(Crypt) resulted in an energy gain of 2.63 eV, and the resultant structure of Al_{12}Cu(Crypt)_2 has the K atom of the second Crypt sitting on top of an Al atom of the Al_{12}Cu cage. The one-electron energy levels of Al_{12}Cu(Crypt)_2 in Figure 6b indicate that an additional electron from the second Crypt has been transferred to fill another empty 2P level of Al_{12}Cu such that the Al_{12}Cu(Crypt)_2 complex now presents a doublet spin state with only one unpaired electron in a 2P^2 electronic configuration and with a small HOMO–LUMO gap of 0.19 eV. The population analysis in this case shows that the Al_{12}Cu core acquires a negative charge of −2.03 electrons from the Crypt molecules, and each Crypt molecule has a positive electronic charge of nearly one electron (Figure 1). Finally, the addition of the third Crypt resulted in an energy gain of 2.2 eV, where the Al_{12}Cu core has a −2.98 charge in the closed-shell Al_{12}Cu(Crypt)_3 species that presented a rather large HOMO–LUMO gap of 1.38 eV. The addition of a fourth Crypt resulted in a smaller energy gain of 1.1 eV and the formation of an Al_{12}Cu(Crypt)_4 less stable species with a smaller HOMO–LUMO gap of 0.27 eV. Further addition of a Crypt resulted in a nonbonded species, showing that the maximum number of Crypt molecules that can bind the Al_{12}Cu core is four. These results are collected in Figure 4c.

We then directed our efforts to explore the potential of the closed-shell Al_{12}Cu(Crypt)_3 species as a resilient building block of ionic assemblies. We prepared several initial orientations of the Al_{12}Cu(Crypt)_3–Al_{12}Cu(Crypt)_3 dimer that were then fully optimized. In this case and for the first time in our studies we found that the Al_{12}Cu(Crypt)_3 units were able to retain their identity toward the formation of the {Al_{12}Cu(Crypt)}_2 dimer, as shown Figure 7, and with a binding energy of 1.41 eV.

Figure 5. Optimized geometries for dimers of the (a) Al_{12}CuK_3 and (b) Al_{12}Cu(K_3O)_3 clusters. Molecular spin multiplicity is given by the superscripts. The relative energies (E_rel) and HOMO–LUMO gaps (HL gap) are also given.
Notably, the assembly is also chemically stable, presenting a large HOMO−LUMO gap of 1.09 eV. Further additions of Al_{12}Cu(Crypt)\textsubscript{3} units to form trimers and tetramers were investigated by approaching the additional Crypt units from the possible orientations and fully optimizing the geometries. We found that as in the case of the dimer both trimer and tetramer resulted in stable assemblies with energy gains of 0.26 and 0.95 eV for the addition of Al_{12}Cu(Crypt)\textsubscript{3} units to the dimer and trimer, respectively. The dimer, trimer, and tetramers also had relatively large HOMO−LUMO gaps of 1.09, 0.97, and 0.93 eV, respectively (Table 1). Most importantly for the formation of stable ionic salts is that the Al_{12}Cu(Crypt)\textsubscript{3} cluster retained its identity in all of the optimized geometries, as shown in Figure 7. On the basis of these results, we confirm that similar to the phosphorus atom in PK\textsubscript{3} the superatom Al_{12}Cu cluster could indeed form truly ionic salts of the Al\textsubscript{12}Cu(Crypt)\textsubscript{3} complex and that assemblies of the Al\textsubscript{12}CuM\textsubscript{3} type hold great potential as building blocks for the development of novel nanostructured materials with tailored properties.

4. CONCLUSIONS
Our theoretical study demonstrates that Al\textsubscript{12}Cu exhibits electronic and chemical behavior similar to that of a phosphorus atom and can be considered its superatom mimic. Al\textsubscript{12}Cu being a 37-valence-electron system corresponds to an open-shell system three electrons short to complete its

### Table 1. Gap between the Highest Occupied and Lowest Unoccupied Molecular Orbitals (HOMO−LUMO gap) for the {Al\textsubscript{12}CuCrypt\textsubscript{x}}\textsubscript{y} (x = 1−4, y = 1−4) Complex\textsuperscript{a}

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<tr>
<td>\textsuperscript{1}Al\textsubscript{12}Cu(Crypt)\textsubscript{0}</td>
<td>0.14</td>
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<tr>
<td>\textsuperscript{2}Al\textsubscript{12}Cu(Crypt)\textsubscript{0}</td>
<td>0.19</td>
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<td>\textsuperscript{3}Al\textsubscript{12}Cu(Crypt)\textsubscript{0}</td>
<td>1.38</td>
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<td>\textsuperscript{4}Al\textsubscript{12}Cu(Crypt)\textsubscript{0}</td>
<td>0.27</td>
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\textsuperscript{a}Molecular spin multiplicity is given by the superscripts.

of stable ionic salts is that the Al\textsubscript{12}Cu(Crypt)\textsubscript{3} cluster retained its identity in all of the optimized geometries, as shown in Figure 7. On the basis of these results, we confirm that similar to the phosphorus atom in PK\textsubscript{3} the superatom Al\textsubscript{12}Cu cluster could indeed form truly ionic salts of the Al\textsubscript{12}Cu(Crypt)\textsubscript{3} complex and that assemblies of the Al\textsubscript{12}CuM\textsubscript{3} type hold great potential as building blocks for the development of novel nanostructured materials with tailored properties.

4. CONCLUSIONS
Our theoretical study demonstrates that Al\textsubscript{12}Cu exhibits electronic and chemical behavior similar to that of a phosphorus atom and can be considered its superatom mimic. Al\textsubscript{12}Cu being a 37-valence-electron system corresponds to an open-shell system three electrons short to complete its
superatomic 2P subshell. It forms ionic compounds with K, K_2O, or Crypt with a high energetic and chemical stability. Our results show that although both K and K_2O provide the required number of electrons, the size of these ions is not large enough to keep strong metal—metal intermolecular interactions from collapsing the cluster during the formation of cluster assemblies. Notably, the larger Crypt ion is found to be the ideal cation to donate the needed electrons and to prevent the Al_{12}Cu core from coalescing. Our studies confirm that similar to the phosphorus atom in PK_3, the superatomic Al_{12}Cu cluster could then form truly ionic salts, as shown from dimers, trimers, and tetramers of the Al_{12}Cu(Crypt)_3 complex calculated from several random possible initial orientations. The integrity of Al_{12}Cu(Crypt)_3 unit in the cluster assemblies shows that the Al_{12}Cu(Crypt)_3 clusters hold a great potential as a building block for the development of novel nanostructured materials.

We believe that the understanding of the interplay between the electronic and geometrical structure and the chemical stability of the investigated systems has the potential to provide a descriptor (or template) toward the computational discovery and design of families of novel nanostructured materials with potential applications. The choice of the Crypt molecules to stabilize the salt opens a route to experimentally generate cluster base ionic salts, and we expect that new ionic assemblies may be developed by extending our findings and that this work motivates experimental investigations that confirm our results.

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