Star-Like CBe₅Au₅⁺ Cluster: Planar Pentacoordinate Carbon, Superalkali Cation, and Multifold (π and σ) Aromaticity

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S Supporting Information

ABSTRACT: We report on the computational design of star-like $CBe_5Au_5^+$ cluster with planar pentacoordinate carbon (ppC), which is also classified as a superalkali cation. Relevant isovalent $CBe_5Au_n^{n-4}$ (n = 2-4), BBe_5Au_5 , and $NBe_5Au_5^{2+}$ clusters with ppC/B/N are studied as well. Global-minimum structures of the clusters are established via computer global searches. The species feature a pentacoordinate pentagonal XBe₅ (X = C, B, N) core, with Au occupying outer bridging positions. Molecular dynamics simulations indicate that they are dynamically stable. Bonding analysis reveals 3-fold (π and σ) aromaticity in $CBe_5Au_5^+$, a key concept that overrides the 18-electron rule and should be applicable for (or help revisit existing models of) other planar



hypercoordinate systems. Vertical electron affinities of $CBe_5Au_5^+$ and its lighter counterparts ($CBe_5Cu_5^+$ and $CBe_5Ag_5^+$) are calculated to be unusually low, which are below 3.89 eV, the smallest atomic ionization potential of any element in the periodic table. Thus, these three clusters belong to superalkali cations. The merge of ppC and superalkali characters makes them unique chemical species.

1. INTRODUCTION

The concept of planar tetracoordinate carbon $(ptC)_{1}^{1}$ a carbon atom bonded with four ligands in an in-plane fashion, was first introduced by Monkhorst in 1968.² The ptC species are usually unstable with respect to their rivals (that is, tetrahedral carbon structures). On the basis of bonding analysis of D_{4h} CH₄, Hoffmann et al.³ proposed in 1970 the "electronic" and "mechanic" strategies to stabilize ptC. In 1976, the first stable ptC molecule, 1,1-dilithiocyclopropane, was predicted by Schleyer and Pople.⁴ Since then, a large number of molecular species with planar tetra-, penta-, hexa-, and hepta-coordinate carbons (ptC, ppC, phC, and p7C) were studied computationally and/or experimentally for over four decades.¹ Notably, a series of simple ptC clusters, NaCAl₄⁻, CAl₃Si⁻, and CAl₃Ge⁻, were observed using photoelectron spectroscopy (PES) by Wang and co-workers.⁵⁻⁷ All of these ptC clusters follow the 18-electron counting.

As a crucial extension of ptC, molecules with planar pentacoordinate carbon (ppC) are also of interest for pursuit. The first ppC and relevant molecules, "hyparenes", were computed by Wang and Schleyer in 2001.⁸ Stimulated by this pioneering work, a number of ppC clusters were explored computationally, including D_{5h} Cu₅H₅C, CBe₅ and CBe₅⁴⁻, CW₅²⁺, and Si₁₀C₂.^{9–12} However, the majority of the species are only local minima, and thus they are merely model clusters and unlikely to be observed in experiments.

A pentagonal D_{5h} CAl₅⁺ cluster represents the first ppCcontaining global minimum (GM), predicted by Zeng and coworkers in 2008.¹³ Similar to the CAl₄²⁻ unit in the ptC NaCAl₄⁻ cluster,⁶ D_{5h} CAl₅⁺ also has 18 valence electrons, although it has remained unclear what is the exact electron-

counting rule for the ptC, ppC, and phC complexes. Following this work and using a simple concept of isoelectronic Be⁻/Al substitution, a series of GM ppC species, CAl₄Be, CAl₃Be₂-, $CAl_2Be_3^{2-}$, and $ECBe_5^{-}$ (E = Al, Ga), were predicted.¹⁴⁻¹⁶ This approach also allowed the generation of multiply charged ppC species, in which intramolecular Coulomb repulsion can be suppressed by counterions. Indeed, the ppC CBe_5^{4-} (or CBe_5) pentagon was stabilized computationally by Li and H,¹⁷ forming $CBe_5Li_n^{n-4}$ and $CBe_5H_n^{n-4}$ (n = 2-5) clusters, which are interesting but not perfect. Molecular dynamics simulations indicate that Li atoms in $CBe_5Li_n^{n-4}$ move irregularly, which interchange bridging positions and even interact with the π cloud. Dynamic stabilities of $CBe_5H_n^{n-4}$ are better. However, both C_s CBe₅H₄ and $C_{5\nu}$ CBe₅H₅⁺ are only quasi-planar, the former being merely a local minimum. How can these deficiencies be overcome and the perfect ppC species be designed? To this end, transition metals may be a good choice, because they have covalent bonding capability that is in between those of Li and H.

The Au element possesses the highest electronegativity (2.54) among all metals, similar to H (2.20), which underlies the isolobal relationship between Au and H, as revealed in silicon auride and boron auride clusters.^{19–22} Now, the open questions are as follows: Can Au atoms stabilize the ppC CBe_5 unit? Are 18-electron BBe_5Au_5 and $NBe_5Au_5^{2+}$ species stable with ppB/N? What are the electron-counting rules that govern the ppC clusters, and what is the nature of bonding therein? In

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Figure 1. Optimized global-minimum structures of $CBe_5Au_n^{n-4}$ (n = 2-5) (1-4), BBe_5Au_5 (5), and $NBe_5Au_5^{2+}$ (6) at the B3LYP/C,Be,B,N/6-311+G(d)/Au/Stuttgart+2f1g level. Bond distances are given in angstroms. Natural atomic charges (in lel) are shown in *italic* in red color.

this contribution, we report a density-functional theory (DFT) study on structural, electronic, and bonding properties of starlike ppC/B/N clusters: $\text{CBe}_5\text{Au}_n^{n-4}$ (n = 2-5), BBe₅Au₅, and NBe₅Au₅²⁺. All species are established as the GM structures via computational global searches, and they also have good dynamic stability. Bonding analysis indicates 3-fold (π and σ) aromaticity, which underlies these unique ppC/B/N clusters. Electronic structure calculations show that CBe₅Au₅⁺ and its lighter congeners (CBe₅Cu₅⁺ and CBe₅Ag₅⁺) have vertical electron affinities (VEAs) below 3.89 eV and can be classified as "superalkali" cations. The evolution of electronic and bonding properties of an extensive series of CBe₅M₅⁺ (M = Li–K, Cu–Au, H, and F–Br) clusters is also discussed.

2. METHODS

The GM structural searches were carried out using the coalescence kick (CK) approach^{23–25} at the hybrid B3LYP/lanl2dz level.^{26,27} Extensive searches were focused on CBe₅Au₅⁺, with over 2100 structures being probed (1370 for singlets and 770 for triplets). For other clusters, only singlets were searched, from 450 to 1000 structures for each species. Top low-lying isomers were reoptimized at the B3LYP/C,Be,B,N/6-311+G(d)/Au/Stuttgart_rsc_1997_ecp+2f1g level.^{28,29} Frequencies were checked at the same level to confirm that the reported structures are true minima. Single-point CCSD(T) calculations^{30–32} were done for top four isomers of CBe₅Au_nⁿ⁻⁴ (n = 2-5) at the B3LYP geometries.

Natural bond orbital (NBO) analyses³³ were performed at the B3LYP/C,Be,B,N/6-311+G(d)/Au/Stuttgart_rsc_1997_ecp+2f1g level. To assess aromaticity, nucleus independent chemical shifts (NICSs)³⁴ were calculated at the centers of three-membered rings and at 1 Å above these centers, as well as at 1 Å above the ppC/B/N centers. Vertical detachment energies (VDEs) and VEAs were calculated using the outer valence Green's function (OVGF) method^{35–37} at the B3LYP and MP2³⁸ geometries. All electronic structure calculations were done using Gaussian 09.³⁹ Molecular structures and canonical molecular orbitals (CMOs) were visualized using CYLview and GaussView 5.0. 40,41

3. RESULTS

3.1. $CBe_5Au_n^{n-4}$ (n = 2-4). Top low-lying structures of $CBe_{s}Au_{n}^{n-4}$ (n = 2-4) clusters (1-3, 1B-1D, 2B-2D, and 3B-3D) are identified from our CK searches; see Figure 1 and the Supporting Information (Figure S1). Among them, 1–3 are the GM structures. Competitive isomeric structures are 1B for $CBe_{5}Au_{2}^{2-}$ and **2B** for $CBe_{5}Au_{3}^{-}$, which are 6.16 and 4.85 kcal mol⁻¹ above their GM structures, respectively, at the singlepoint CCSD(T) level with zero-point energy (ZPE) corrections at B3LYP. Other isomers (1C-1D, 2C-2D, and **3B–3D**) turn out to be at least 17 kcal mol⁻¹ higher in energy. In particular, the nearest low-lying isomer of CBe_5Au_4 (3B) is located at 32.45 kcal mol⁻¹, suggesting that 3 as GM is welldefined on the potential energy surface. In all 12 low-lying structures, the Au atoms are situated far away from the C center, serving as terminals or bridges. This observation is in line with the Au/H isolobal analogy. $^{19-22}$ Au–Au interaction, if any, may be present in isomers 2D and 3D.

GM structures 1–3 of $\text{CBe}_5\text{Au}_n^{n-4}$ (n = 2-4) are illustrated in Figure 1, along with their bond distances and NBO atomic charges. All three species are perfectly planar and feature a pentagonal CBe₅ core, with from two to four bridging Au atoms on the periphery. The C–Be bond distances are 1.72–1.76 Å in 1, 1.66–1.76 Å in 2, and 1.69–1.78 Å in 3, which indicate reasonably strong C–Be bonding. As a reference, the upper bound of a single C–Be bond is 1.77 Å based on the recommended covalent atomic radii.⁴² Unevenness of C–Be distances in 1–3 is due to asymmetric Au coordination, as anticipated. There is a trend that Au coordination slightly shortens C–Be distances in the vicinity. Thus, a C–Be bond associated with two Au bridges is apparently shorter than others.

For the Be–Be links in 1-3, those without an Au bridge are 1.89-1.96 Å, whereas those with an Au bridge are 2.05-2.18 Å.

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Table 1. Calculated Lowest Vibrational Frequency (ν_{\min}) of CBe₅Au_nⁿ⁻⁴ (n = 2-5), BBe₅Au₅, and NBe₅Au₅²⁺ Clusters (1-6) at the B3LYP/C,Be,B,N/6-311+G(d)/Au/Stuttgart rsc 1997 ecp+2f1g level, along with Wiberg Bond Index (WBI) of C/B/N-Be, Be-Be, and Be-Au Bonds and Total WBI of C/B/N, Be, and Au Atoms

species ^a		1	2	3	4	5	6
$ u_{ m min}~(m cm^{-1})$		83	58	22	18	21	8
WBI _{C/B/N-Be}	Be _a	0.51	0.60	0.62	0.55	0.68	0.39
	Beb	0.53	0.55	0.58			
	Be _c	0.54	0.50	0.48			
WBI _{Be-Be}	a-b ^b	0.77	0.27	0.28	0.30	0.31	0.33
	b-c	0.27	0.82	0.29			
	c-c	0.81	0.27	0.81			
WBI _{Be-Au}	Be _a		0.60	0.58	0.60	0.59	0.62
	Beb	0.66	0.56	0.59/0.62			
	Be _c	0.62	0.61	0.58			
WBI _{C/B/N}		2.75	2.82	2.86	2.90	3.52	2.07
WBI _{Be}	Bea	2.49	2.52	2.49	2.49	2.64	2.38
	Beb	2.45	2.43	2.50			
	Be _c	2.51	2.43	2.37			
WBI _{Au}	ab ^c		1.35	1.34	1.34	1.33	1.36
	bc	1.60		1.34			
	сс		1.37				

"Atomic labels "a", "b", and "c", as shown in Figure 1. "Labels "a-b", "b-c", and "c-c" denote the Bea-Beb, Beb-Bec, and Bec-Bec links, respectively. "Labels "ab", "bc", and "cc" define the positions at which a bridging Au atom is situated.

Clearly, an Au bridge elongates the Be-Be bond. We stress that Be-Be interactions in the clusters are substantial. A Be₂ dimer is van der Waals type (2.45 Å),⁴³ and a Be_2^+ cluster with a half bond is 2.21 Å.⁴⁴ Be-Be bonds in 1-3 are thus comparable to, or stronger than, that in Be2⁺ cation. The Au-Be distances are uniform (2.22–2.26 Å), indicating quite strong bonding (upper bound of Au-Be single bond: 2.26 Å).42 Calculated Wiberg bond indices (WBIs; Table 1) from NBO analyses for 1-3 are in line with the above assignments.

3.2. $CBe_5Au_5^+$, BBe_5Au_5 , and $NBe_5Au_5^{2+}$. D_{5h} $CBe_5Au_5^+$ (4), BBe_5Au_5 (5), and $NBe_5Au_5^{2+}$ (6) are perfectly planar, starlike clusters with a ppC/B/N center, as illustrated in Figure 1. These species are isovalent, because $C^+/B/N^{2+}$ have the same number of electrons. According to the CK global searches, D_{5h} $CBe_5Au_5^+$ (4) is well-defined as GM (Figure S1), with the nearest isomer 4B being 23.05 kcal mol⁻¹ above it. We also briefly examined the CBe₅Au₅ neutral cluster. Its star-like structure is slightly nonplanar and distorted to C_s symmetry, yet it remains the lowest in energy as compared to alternative neutral conformations based on 4B-4D.

Clusters 4-6 may be described as an inner wheel-like XBe₅ (X = C, B, N) core interacting with an outer Be₅Au₅ ring. The Au-Be distances are even in three species (2.18-2.24 Å). The X-Be distances are 1.80, 1.73, and 1.72 Å from B to N, which correlate to the decrease of atomic radius along the series (0.82, 0.77, and 0.70 Å for B, C, and N, respectively). Note that Coulomb repulsion in dication 6 should counter the shrink of N-Be distance. The nature of X-Be, Be-Be, and Be-Au bonding in 4-6 is qualitatively similar to that in 1-3 (section 3.1), except that the latter species have uneven bonds due to asymmetric Au coordination.

3.3. Molecular Dynamics. Thermodynamic stability benefits the star-like ppC/B/N species for potential synthesis in the gas phase. However, it is not enough. Thus, Born-Oppenheimer molecular dynamics (BOMD) simulations were performed for clusters 1-6 at the B3LYP/lanl2dz level, for 30 ps at room temperature (298 K). All of the 1-6 species maintain structural integrity during BOMD simulations (Figure

S2), suggesting that these clusters are robust against isomerization and decomposition. Figure 2 compares the dynamics of



Figure 2. Root-mean-square deviations (RMSDs) of $C_{2\nu}$ CBe₅Au₂²⁻ (1) during the molecular dynamics (MD) simulation at 298 K, as compared to those of $C_{2\nu}$ CBe₅H₂²⁻.

 $CBe_5Au_2^{2-}$ (1) and its isoelectronic $CBe_5H_2^{2-}$ species¹⁸ for up to 100 ps. While 1 is dynamically stable against Au migration to neighboring bridging sites, H-migration is frequently observed for $CBe_5H_2^{2-}$ at room temperature. Thus Au seems to be superior to H in terms of stabilizing the ppC CBe₅ unit, intuitively due to the heavy mass of the Au atom.

4. DISCUSSION

4.1. Star-Like ppC/B/N Clusters: $CBe_5Au_n^{n-4}$ (n = 2-5), BBe₅Au₅, and NBe₅Au₅²⁺. The CBe₅Au_nⁿ⁻⁴ (n = 2-5), BBe₅Au₅, and NBe₅Au₅²⁺ clusters (1-6) possess a similar planar pentacoordinate XBe_5 (X = C, B, N) unit as structural core. Au atoms occupy peripheral positions as bridging ligands, successively building up a series of star-like clusters, in which the XBe₅ core maintains its structural integrity. The X-Be and Be-Be distances within the XBe_5 core in 1-6 follow the intuitive trend with the change of X or n, where asymmetric coordination of n Au ligands induces only a slight variation in



Figure 3. Analysis of canonical molecular orbitals (CMOs) of D_{5h} CBe₅Au₅⁺ (4) cluster. (a) Orbital energy diagram and HOMO–LUMO energy gap; (b) 10 σ subsystem derived from C/Be 2s atomic orbitals (AOs); (c) 2π subsystem; (d) 6σ subsystem with primary contributions from Au 6s AOs. The analysis indicates 3-fold aromaticity for 4.

bond distances (Figure 1). The fact that Au prefers bridging sites supports the concept of Au/H isolobal analogy.¹⁹⁻²²

In terms of valence electrons, clusters 1-6 all contain 18 electrons, balanced by overall charges from 2– to 2+. The 18electron counting appears to be a "magic" rule for ppC/B/N, although this counting is by no means the same as the traditional 18-electron rule in three-dimensional compounds. In fact, model phC complex CB_6^{2-} has 24 electrons,⁸ suggesting that 18 electrons are not necessarily a rule for planar hypercoordinate clusters.^{45–47} As we will show below via bonding analysis, 18-electron counting in 1-6 can be elucidated using the concept of 3-fold (π and σ) aromaticity.

Note that, upon Au coordination, WBI for Be–Be in 1–6 decreases from ~0.8 to ~0.3, which hints that the Au bridge breaks Be–Be bonding and facilitates Be–Au–Be bonding (Table 1). It is also interesting to note that, in $\text{CBe}_5\text{Au}_n^{n-4}$ (n = 2-5), BBe_5Au_5 , and $\text{NBe}_5\text{Au}_5^{2+}$, all C/B/N centers persistently carry a natural charge of ~2 lel, independent of X, Au, or overall charge (Figure 1). The observation suggests that this natural charge is primarily due to Be–X interaction within the XBe₅ core and has little to do with Au ligands or extra charges.

4.2. Chemical Bonding in ppC/B/N Complexes: 3-Fold (π and σ) Aromaticity. The bonding in ppC/B/N complexes may be understood via CMO analysis, aided with orbital composition calculations.⁴⁸ Since the essence of bonding is similar in star-like 4–6 species,⁴⁹ we use D_{5h} CBe₅Au₅⁺ (4) as an example. The energy level diagram of 4 is presented in Figure 3. The nine occupied CMOs can be sorted in three subsets. Subset 1 (Figure 3b) has five CMOs primarily derived from C/Be 2s atomic orbitals (AOs): HOMO–20 (a₁'), HOMO–19 (e₁'), and HOMO–1 (e₂'). This subset of CMOs has zero, 1, and 2 nodal planes; LUMO (e₂') are the next along this series (3 nodal planes). These CMOs have substantial contributions from the CBe₅ core, from 97% in HOMO–20, 66% in HOMO–19, to 34% in HOMO–1. In other words,

they form a 10 σ disk-delocalization system primarily in the CBe₅ core, akin to the 6σ delocalization in the D_{7h} B₈^{2–} molecular wheel.⁵⁰ Subset 2 (Figure 3c) is the π framework and involves only the HOMO. The 2π electrons are also contributed mainly by CBe₅ (85%). Lastly, subset 3 (Figure 3d) is a 6σ system with major contributions from Au 6s AOs: 75% for HOMO–3 (a₁') and 51% for HOMO–2 (e₁'). Additional contributions from Be₅ amount to 22 and 23%, respectively. Therefore, subset 3 may be assigned mainly to the outer Be₅Au₅ ring.

In short, D_{5h} CBe₅Au₅⁺ (4) has three σ and π subsystems (10 σ , 2π , and 6σ), which are mutually orthogonal to each other.⁵¹ None of the subsystems can be localized as classical Lewis bonds. Thus, they indicate 3-fold delocalization in 4, that is, 3-fold (π and σ) aromaticity. This bonding picture is depicted in Figure 4, which overrides the 18-electron rule.^{45–47}



Figure 4. Bonding model for $D_{5h} \operatorname{CBe}_{5}\operatorname{Au}_{5}^{+}(4)$ and relevant isovalent species.

Note that 10σ , 2π , and 6σ electron-counting all conform to the (4n + 2) Hückel rule.^{52–57} NICS calculations³⁴ offer an independent probe for aromaticity. NICS(0) and NICS(1), calculated at the ring center and 1 Å above it, characterize σ and π aromaticity, respectively. The NICS values for cluster 4 are shown in Figure S3. Both NICS(0) and NICS(1) are highly negative, fully supporting the idea of π and σ aromaticity.

It is stressed that, while the 10σ subsystem is ascribed primarily to the CBe₅ core (60%), it also has components from Au₅ (by about 40%). In our opinion, it is thus oversimplified to describe D_{5h} CBe₅Au₅⁺ (4) as an inner CBe₅ core plus an outer Be₅Au₅ ring. The 10σ subsystem is essentially global in nature and glues the CBe₅ core and outer Be₅Au₅ ring as an integral star-like cluster. This bonding picture may apply for all star-like clusters **1–6**, as well as relevant CBe₅M₅⁺ (M = H, Li–K, F– Br) species in prior reports.⁵⁸

4.3. Planar Pentacoordinate Carbons Meet Superalkalis: Electronic Properties of the $CBe_5M_5^+$ (M = Li–K, Cu–Au, H, and F–Br) Series. The ppC species are unique in physical chemistry.¹ It is of interest to explore the electronic structure of these star-like ppC/B/N clusters. As an example, the orbital energy diagram of 4 is shown in Figure 3a. The density of state is high near the HOMO, with five CMOs being spaced within ~0.5 eV. The LUMO and HOMO are separated by a sizable energy gap, suggesting that 4 as a cation is electronically robust. This is understandable because 4 is an 18electron system and its neutral counterpart has 19 electrons. Thus, $D_{5h} CBe_5Au_5^+$ (4) may mimic an alkali metal cation.

Quantitatively, the VEA of D_{5h} CBe₃Au₅⁺ (4) is calculated to be 3.75 and 3.82 eV at OVGF//B3LYP and OVGF//MP2, respectively, which is the ionization potential (IP) of the starlike CBe₃Au₅ neutral cluster. The IP is even smaller than that of the Cs atom (3.89 eV), the lowest of any element in the periodic table. Following the definition, cluster 4 can be classified as a superalkali cation.⁵⁹ In fact, the star-like CBe₃Au₅ neutral is also competitive on its potential energy surface. Note that C, Be, and Au atoms in 4 possess IPs of 11.26, 9.32, and 9.22 eV, respectively, far greater than 3.75/3.82 eV. The unexpected, low VEA of 4 has to be due to collective effect in the cluster. We believe 3-fold (10 σ , 2π , and 6σ) aromaticity holds the key for this, which generates a sizable HOMO– LUMO gap in 4 and destabilizes its LUMO. Nevertheless, this is not the complete truth.

In fact, even $C_{2\nu}$ CBe₅Au₃⁻ (2), a closed-shell 18-electron anion, exhibits unusual properties. Intuitively, one expects that 2 has high binding energies and its neutral species probably belongs to superhalogens.⁶⁰ Our simulated PES spectrum of 2 counters this idea, with a ground-state VDE of only 2.55 eV (Figure S4). Furthermore, the first two PES bands are separated from higher ones by a gap of ~1.8 eV. The PES pattern correlates to the nature of frontier CMOs (Figure S5). Here, HOMO and HOMO-1 are derived from Be 2s AOs (by 88%) and can be recombined for two-center two-electron (2c-2e) Be–Be σ bonds. Such CMOs are anticipated to have lower binding energies with respect to C/Au based ones. Indeed, HOMO-2 is a completely bonding π CMO with major contribution from C 2p AO (67%), whereas HOMO-3 through HOMO-5 are Au 6s based.

It is valuable to examine the evolution of electronic properties of the $CBe_5M_5^+$ (M = Li-K, Cu-Au, H, and F-Br) series, in which M spans a diverse range from alkali metals, coinage metals, hydrogen, to halogens. Similar to $CBe_5Au_5^+$, star-like ppC $CBe_5Cu_5^+$ and $CBe_5Ag_5^+$ species are the GM structures on their potential energy surfaces according to our CK searches. For other $CBe_5M_5^+$ species, $CBe_5H_5^+$ was recently computed¹⁸ to be a pseudo-superalkali cation and $CBe_5M_5^+$ (M = Li-K, F-Br)⁵⁸ belong to superalkali cations. In all of these star-like species, the concepts of ppC and superalkali merge in a single system, which are unique considering that both ppC and superalkali are unconventional chemical ideas.^{1,59} Comparative

data of the whole series are collected in Figure 5 as well as in Tables 2 and S1. While the IP of atom M spans from 4.34 to



Figure 5. Evolution of (a) vertical electron affinity (VEA), calculated at the OVGF//MP2 level, of the $CBe_5M_5^+$ (M = Li–K, Cu–Au, H, and F–Cl) series as a function of M. The atomic ionization potential (IP; experimental data) of M is also plotted for comparison. Shown in part b is the energy drop between VEA and IP as a function of M. The curves offer insight into bonding along this series of complexes.

17.42 eV, VEAs of $CBe_5M_5^+$ (M = Li–K, Cu–Au, H, and F–Br) drop markedly and are below 3.89 eV, except for $CBe_5H_5^+$ (Figure 5a). The magnitude of IP drop amounts to 2.88–2.23 eV for Li–K, 3.83–5.41 eV for Cu–Au, 9.57 eV for H, and 13.68–8.73 eV for F–Br (Figure 5b). In particular, IP drop for the H/F/Cl/Br species is significant.

A key point to rationalize this trend lies in the fact that the ppC species are all 18-electron systems with multifold aromaticity (10 σ , 2 π , and 6 σ). As typical examples, CMOs of $CBe_5K_5^+$ and $CBe_5H_5^+$ are analyzed in Figure 6,⁶¹ which resemble those of $CBe_5Au_5^+$ (4) (Figure 3). The bonding pattern dictates that frontier CMOs of the ppC species are similar in nature, although not necessarily identical; see Table S2. Indeed, the shapes of the LUMO differ from species to species: Na/K (Na/K s based), Li/Cu/Ag/Au (Be based σ CMO), H/Br/Cl (Be based π CMO), and F (Be based, completely bonding σ CMO). However, the LUMO is Be based for the majority of the species (from 63 up to 100%), plus two species that are K/Na based (90-92%). Thus, the VEA of CBe₅M₅⁺ clusters has little relevance to M. Rather, it is associated with the Be5 ring and should be low for all species (see also Figure S5). On the basis of this understanding, the exact nature of M merely serves as a perturbation to VEA, which explains why all of these ppC clusters are superalkali cations. Lastly, orbital components of the LUMO also hint that Be/Li and Be/Au bonding are remarkably covalent (Table S2). Note that even the $CBe_5Cl_5^+$ and $CBe_5Br_5^+$ species appear to be more covalent than anticipated (Table 2), in which Cl_5 and Br_5 collectively carry a charge of only -0.58 and -0.10 lel, respectively.

Table 2. Calculated Vertical Electron Affinities (VEAs), Vertical Detachment Energies (VDEs), and HOMO–LUMO Gaps of the $CBe_5M_5^+$ (M = Li–K, Cu–Au, H, F–Cl) Series at the Outer Valence Green's Function (OVGF) Level, Using the B3LYP and MP2 Optimized Structures^a

species	VEA ^b	VDE ^b	$E_{\rm HOMO-LUMO}^{b}$	$q (M_5)^c$	$q (Be_5)^c$	<i>q</i> (C) ^{<i>c</i>}
CBe ₅ Li ₅ ⁺	2.51 (2.51)	8.89 (8.82)	6.92	4.18	-1.11	-2.07
CBe ₅ Na ₅ ⁺	2.35 (2.36)	8.00 (7.92)	6.19	4.02	-0.83	-2.19
CBe ₅ K ₅ ⁺	2.11 (2.11)	6.69 (6.74)	4.99	4.32	-1.05	-2.27
CBe ₅ Cu ₅ ⁺	3.80 (3.90)	11.55 (11.56)	8.48	2.28	0.71	-1.99
CBe ₅ Ag ₅ ⁺	3.46 (3.55)	11.26 (11.28)	8.34	2.39	0.67	-2.06
CBe ₅ Au ₅ ⁺	3.75 (3.82)	12.45 (12.23)	8.97	1.31	1.72	-2.03
CBe ₅ H ₅ ⁺	4.07 (4.03)	14.39 (14.21)	11.07	-1.02	3.81	-1.79
CBe ₅ F ₅ ⁺	3.74 (3.74)	13.77 (13.66)	10.84	-2.87	5.97	-2.10
CBe ₅ Cl ₅ ⁺	3.03 (3.01)	12.95 (12.82)	11.08	-0.58	3.45	-1.87
CBe ₅ Br ₅ ⁺	3.09 (3.08)	12.76 (12.65)	11.05	-0.10	3.07	-1.97

"Also listed are natural atomic charges (q; in lel) from the natural bond orbital (NBO) analysis. ^bCalculated at the OVGF//B3LYP and OVGF// MP2 (in *italic*) levels, respectively. All energies are in eV. ^cNBO analysis at the B3LYP/C,Be,Li,Na,K,F,Cl,Br/6-311+G(d)/H/6-311+G(d,p)/ Cu,Ag,Au/Stuttgart+2f1g level.



Figure 6. CMOs of (a) D_{5h} CBe₅K₅⁺ and (b) D_{5h} CBe₅H₅⁺ clusters. The CMOs are sorted into 10 σ , 2π , and 6σ subsystems, similar to those in D_{5h} CBe₅Au₅⁺ (4) (Figure 3).

5. CONCLUSIONS

We have designed, via computer global searches, a star-like $CBe_{s}Au_{s}^{+}$ cluster with planar pentacoordinate carbon (ppC). Relevant isovalent ppC/B/N species, CBe₅Au_nⁿ⁻⁴ (n = 2-4), BBe₅Au₅, and NBe₅Au₅²⁺, are also explored. These clusters have star-like geometries with a pentacoordinate XBe_5 (X = C, B, N) core. Bonding analysis suggests that the CBe₅Au₅⁺ cluster as an 18-electron system can be subdivided into three subsystems $(10\sigma, 2\pi, \text{ and } 6\sigma)$, each conforming to the (4n + 2) Hückel rule. The star-like clusters thus have 3-fold (π and σ) aromaticity, a key understanding for planar hypercoordinate chemistry in general, which underlies the unusual ppC/B/N coordination. Electronic structure calculations show that vertical electron affinities (VEAs) of CBe₅Au₅⁺ and its lighter congeners (CBe₅Cu₅⁺ and CBe₅Ag₅⁺) are below 3.89 eV, making them superalkali cations. The ppC clusters with superalkali cation properties are intriguing and unique in coordination and physical chemistry.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.7b11789.

Cartesian coordinates for optimized structures of clusters **1–6**, three low-lying isomers nB-nD (n = 1-4), $CBe_5Cu_5^+$, and $CBe_5Ag_5^+$ at the B3LYP level; orbital composition of the LUMO of $CBe_5M_5^+$ (M = Li-K, Cu-Au, H, F-Br); optimized structures of global minima **1–4** and their three lowest-lying isomers at B3LYP; RMSDs of **1–6** during BOMD simulations at 298 K; calculated NICSs for clusters **1–6**; simulated photoelectron spectrum of $C_{2\nu}$ $CBe_5Au_3^-$ (**2**) anion cluster using the TD-B3LYP method; and frontier CMOs and energy level diagram of **2** (PDF)

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Notes

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They differ only in the spatial distribution of the σ/π bonds; see Figures 3 and 6. For alkali metal based species, electron clouds shrink to the CBe₅ core. For halogen based species, outer clouds lean more to the M₅ centers. In CBe₅Li₅⁺, CBe₅H₅⁺, and CBe₅Au₅⁺ clusters, the Be–M bonding is covalent and electron clouds are spread over all 11 atoms.