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Reactivity, Selectivity, and Aromaticity of Be_3^{2-} and Its Complexes

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The stability, reactivity, and aromaticity of the Be_3^{2-} dianion and its bimetallic species are investigated. The aromaticity of these systems is analyzed in the light of the DFT-based reactivity descriptors, namely, hardness (η) and polarizability (α), molecular orbital (MO) analysis, and the nucleus-independent chemical shift (NICS). The recently discovered direct Zn−Zn bond is stabilized through the complexation with Be_3^{2-}, and a new compound $[(Be_3)_2Zn_2]^{2-}$ is reported. The chemical nature and selectivity of the Be_3^{2-} unit in its bimetallic form are analyzed using the atomic charge (Q_k) and nucleophilicity excess ($\Delta\omega_g^{\mp}$) descriptors to examine its applicability in the field of molecular electronics.

Introduction

The concept of aromaticity[1,2] has been extended to the all-metal molecules through the discovery of the square-planar Al_4^{2-} unit in bimetallic MAl_4^{2-} (M = Li, Na, Cu) species.[3] Later on, many such all-metal aromatic species,[4−15] for example, M_4^{2-} (M = Ge, In, Tl, Sb, Bi),[4] M_4^{2+} (M = Se, Te),[5] Hg_4^{6-},[6] M_5^- (M = Sb, Bi),[7] M_5^{6-} (M = Ge, Sn, Pb),[8] Au_5Zn^+,[9] Al_6^{2-},[10] and so forth, have come to the fore through experimental/theoretical investigations. Aromatic trigonal molecules, for example, M_3^- (M = Al, Ga),[11] X_3^- (X = Sc, Y, La),[12a] X_3^+ (X = H, Li, Na, K, Cu),[12b] MX_3 (M = Li, Na, K; X = Sc, Y, La),[12a] and XCl_3 (X = H, Li, Na, K, Cu),[12b] are also reported. The anion of Be_n^- ($n = 2, 3$) has been obtained experimentally,[14] and a theoretical investigation on their stability has been also done.[15] Recently, π-aromaticity of Be_3^{2-} molecule was presented.[16] The existence and reactivity of the sandwich complexes of many of those aromatic units, for example, MAl_4TiMAl_4 (M = Li, Na, K),[17,18] have also gained a lot of attention. Density functional theory (DFT)[19,20] has played an important role in predicting stability, reactivity, and aromaticity in such all-metal molecules along with the organic[21] and inorganic[18,22,23] molecules.

Density functional theory (DFT)[19,20] based global and local reactivity descriptors, for example, electronegativity (χ),[24] hardness (η),[25] polarizability (α),[26] electrophilicity (ω),[27,28] philicity,[29] and so forth, are found to be useful in explaining the various physicochemical processes/properties, for example, reaction mechanism,[30] acidity/basicity,[31] biological activities[32] and toxicity[33,34] of a diverse class of molecules, as well as aromaticity.[18,21−23] These descriptors may be properly understood in terms of their related electronic structure principles, namely, the electronegativity equalization principle,[35] the hard−soft acid−base (HSAB) principle,[36,37] the maximum hardness principle (MHP),[38,39] the minimum polarizability principle (MPP),[40] the minimum electrophilicity principle (MElP),[41] and so forth. The electronegativity equalization principle[35] is stated as, "During an electron-transfer process in a chemical reaction, electrons flow from a species of lower electronegativity (higher chemical potential) to one with higher electronegativity (lower chemical potential) until the electronegativities get equalized to a value approximately equal to the geometric mean of the electronegativities of the isolated species". The hard−soft acid−base (HSAB) principle,[36,37] which, in general, describes a variety of chemical reactions, may be stated as, "Hard acids prefer to coordinate with hard bases, and soft acids prefer to coordinate with soft bases for both their thermodynamic and kinetic properties". The maximum hardness principle (MHP)[38,39] is stated as, "There seems to be a rule of nature that molecules arrange themselves so as to be as hard as possible". The minimum polarizability principle (MPP)[40] may be expressed as, "The natural direction of evolution of any system is toward a state of minimum polarizability". The minimum electrophilicity principle (MElP)[41] may be stated as, "Electrophilicity will be a minimum (maximum) when both chemical potential and hardness are maxima (minima)".

Various physicochemical properties, for example, stability, bonding, reactivity, and aromaticity of the sandwich complexes of the metallacenes, form a great point of interest.[42−50] The recent discovery of the first direct metal−metal-bonded Zn_2^{2+} by Resa et al. (2004)[46] is one of the most exciting developments in organometallic chemistry. They isolated Zn_2^{2+} in a compound, decamethyldizincocene, $Zn_2(\eta^5\text{-}C_5Me_5)_2$, which was obtained unexpectedly from the reaction of $(\eta^5\text{-}Me_5C_5)_2Zn$ with Et_2Zn. A number of experimental/theoretical investigations have been carried out to predict the structure and reactivity of the other possible direct metal−metal-bonded analogue of the original synthesized compound, for example, $M_2(\eta^5\text{-}Cp)_2$ (Cp = $Me_5C_5^-$/$C_5H_5^-$; M = Cd, Hg, Ni, Cu, Be).[47−50]

Monometallic super atoms with the form of M_n^q, where M is a metal like Au, Ag, Si, Al, Ga, and so forth and q is the molecular charge, and their bimetallic species have gained a lot of attention for the synthesis, characterization, and design of materials applicable to human development.[51−54] A rigorous effort has been assigned to design and apply these metal units as building blocks of the electrode (lead) in molecular electronic devices, for example, molecular rectifiers, semiconductors, and transistors.[51−54] For this purpose, the understanding of the chemical nature and reactivity of these building blocks is important.[51−55]

In the present work, we have investigated the possible stable geometries of the Be_3^{2-} dianion unit and its bimetallic species

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MBe_3^- (M = Li, Na, Cu) and M_2Be_3 (M = Li, Na, Cu). The aromaticity of these molecules is investigated in terms of DFT-based new aromaticity indices ΔX [$X = E$, α, η],[18] molecular orbital (MO) analysis, and the nucleus-independent chemical shift (NICS) values.[13b,56] The potency of the Be_3^{2-} (D_{3h}) unit in stabilization of a direct zinc−zinc bond is also investigated through the substitution reaction of Cp ($=C_5H_5^-$) by the Be_3^{2-} unit. Also, aromaticity in the Cp and Be_3^{2-} rings in the Cp_2Zn_2 and $[(Be_3)_2Zn_2]^{2-}$ compounds, respectively, has been inquired in light of NICS. Finally, an investigation on the suitability of the Be_3^{2-} unit in its bimetallic species, and the direct Zn−Zn bonded sandwich compound, $[(Be_3)_2Zn_2]^{2-}$, in application to the molecular electronics is performed.

Theoretical Background

Electronegativity[24] (χ) (negative of the chemical potential[57] (μ)) and chemical hardness[25] (η) for an N-electron system are defined quantitatively as the first- and second-order number derivatives of total energy (E), respectively, as follows

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_{\upsilon(\vec{r})} \quad (1)$$

$$\eta = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right)_{\upsilon(\vec{r})} = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{\upsilon(\vec{r})} \quad (2)$$

where $\upsilon(\vec{r})$ is the external potential.

Using a finite difference approximation, the above definitions may be expressed as[25,57]

$$\chi = \frac{I + A}{2} \text{ and } \eta = \frac{I - A}{2} \quad (3)$$

where I and A are the ionization potential and the electron affinity, respectively.

The ionization potential (I) and electron affinity (A) for an N-electron system may be expressed using the ΔSCF finite difference approach as follows

$$I \approx E\,(N-1) - E\,(N) \qquad A \approx E\,(N) - E\,(N+1) \quad (4)$$

where $E(N)$ is the electronic energy for the N-electron system.

The binding energy is defined as the difference between the total energies of the products and reactants in a chemical reaction. For an anionic system, the adiabatic electron affinity (ΔE_e) is equal to[15]

$$\Delta E_e = E_n(N) - E_a(N + 1) \quad (5)$$

as in eq 4, where n and a denote the electronic states of the neutral and the charged systems, respectively. For example, for the ground state of a system, n and a are equal to zero. For the calculation of the adiabatic electron affinity (ΔE_e) from eq 5, one has to calculate both the energies of the neutral and the charged systems at their respective equilibrium structures.[15]

The electrophilicity index (ω), which measures the stabilization in energy when a system acquires an additional electronic charge from the environment is defined by Parr et al. as[27]

$$\omega = \mu^2/2\eta \quad (6)$$

where μ and η are the chemical potential and hardness, respectively.

As proposed by Yang and Mortier,[58] the condensed Fukui function (FF) may be expressed based on a finite difference method as follows

$$f_k^+ = q_k(N+1) - q_k(N) \quad \text{for nucleophilic attack} \quad (7a)$$

$$f_k^- = q_k(N) - q_k(N-1) \quad \text{for electrophilic attack} \quad (7b)$$

$$f_k^o = [q_k(N+1) - q_k(N-1)]/2 \quad \text{for radical attack} \quad (7c)$$

where q_k is the electronic population of atom k in a molecule.

Chattaraj et al.[29] proposed the generalized concept of philicity, which contains almost all information on the global and local issues of a molecule as well as the nucleophilic/electrophilic power of a given atomic site. The philicity at any atomic site k is defined as

$$\omega_k^\alpha = \omega \cdot f_{\mathrm{k}}^\alpha \quad (8)$$

where (α = +, −, and 0) represents local philic quantities describing nucleophilic, electrophilic, and radical attacks.

The group philicity, which is the sum of the individual philicities over a group of relevant atoms, may be expressed as[59]

$$\omega_g^\alpha = \sum_{k=1}^{n} \omega_k^\alpha \quad (9)$$

where n is the number of atoms coordinated to the reactive atom, ω_k^α is the local electrophilicity of the atom k, $\omega_{\mathrm{g}}^\alpha$ is the group philicity obtained by adding the local philicity of the nearby bonded atoms, and (α= +, −, 0) represents nucleophilic, electrophilic, and radical attacks, respectively.

Recently, a new local reactivity descriptor, nucleophilicity excess, or net nucleophilicity ($\Delta\omega_{\mathrm{g}}^{\mp}$) is proposed along the line of the dual descriptor[60] to account for the nucleophilic or electrophilic nature of a group of atoms or a part of a molecule as[55,61]

$$\Delta\omega_g^{\mp} = \omega_g^- - \omega_g^+ = \omega(f_{\mathrm{g}}^- - f_{\mathrm{g}}^+) \quad (10)$$

where

$$\omega_g^- \equiv \sum_{k=1}^{n} \omega_k^-$$

and

$$\omega_g^+ \equiv \sum_{k=1}^{n} \omega_k^+$$

are the group philicities of the nucleophile/electrophile in the molecule due to electrophilic and nucleophilic attacks, respectively. For a nucleophile, $\Delta\omega_{\mathrm{g}}^{\mp}$ is expected to be positive, while it should be negative for an electrophile in a molecule.

The nucleofugality, $\Delta E_{\mathrm{nucleofuge}}$, is used to quantify the nucleophilic capabilities of a leaving group, which is defined as[62]

$$\Delta E_{\mathrm{nucleofuge}} = \frac{(I - 3A)^2}{8(I - A)} \quad (11)$$

where I and A are the ionization potential and electron affinity, respectively.

The electric dipole polarizability (α) is represented as the second-order variation in energy with respect to the electric field $\mathbf{F}$ as

$$\alpha_{a,b} = -\left(\frac{\partial^2 E}{\partial F_a \partial F_b}\right) \quad a,b = x, y, z \quad (12)$$

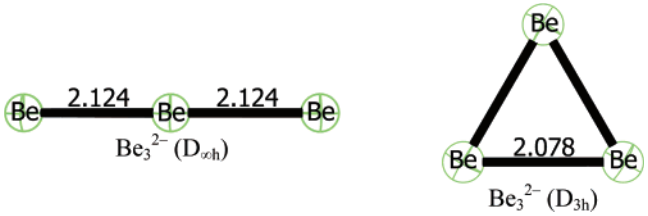

Figure 1. Optimized geometries of the open and closed isomers of Be_3^{2-}.

TABLE 1: Relative Energy (ΔE), Relative Polarizability ($\Delta\alpha$), Relative Hardness ($\Delta\eta$), Relative Electrophilicity ($\Delta\omega$), and Relative Nucleofugality (ΔE_n) Values for Various Isomers of Be_3^{2-}

Be_3^{2-}	closed isomer Be_3^{2-} (D_{3h})	open isomer Be_3^{2-} ($D_{\infty h}$)	$\Delta X = X_{Closed} - X_{Open}$ ($X = E, \alpha, \eta, \omega, \Delta E_n$)
E^a (Rel. E)	−44.0034 (0.0)	−43.9842 (0.0192)	−0.0192
α^a	357.0103	943.4553	−586.4450
η^b	0.9144	0.8518	0.0626
ω^b	8.7025	7.6324	1.0701
$\Delta E_n{}^b$	9.2551	8.2738	0.9813

[a] In au. [b] In eV.

which is a measure of the linear response of the electron density in the presence of an infinitesimal electric field **F**.

The polarizability α is calculated as the mean value as given in the following equation

$$\langle\alpha\rangle = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3 \tag{13}$$

The nucleus-independent chemical shift (NICS)[13b,56] is defined as the absolute magnetic shielding computed at the center of a ring in a molecule. NICS(0) and NICS(1) are calculated at the center and 1 Å above the ring, respectively.

Computational Details

The geometries of Be_3^{2-}, Be_3^-, Be_3, Be_2^-, and Be_2 molecules and various related bimetallic species, for example, MBe_3^- (M = Li, Na, Cu) and M_2Be_3 (M = Li, Na, Cu) are minimized at the B3LYP/6-311+G(d) level of theory using the G03W[63] program. Harmonic vibrational frequency analysis is also performed at the same level of theory to find out the minima in the potential energy surface. Structures of the Cp ($C_5H_5^-$, D_{5h}), Cp_2Zn (C_S), $CpZn_2Cp$ (D_{5h}), and $[Be_3Zn_2Be_3]^{2-}$ (D_{3h}) are optimized at the B3LYP/6-311+G(d) level, and the corresponding frequency analysis is also performed at the same level of theory. The energetically most stable C_S symmetry[64] for the Cp_2Zn molecule is considered in the present study. All of the molecules considered here possess zero number of imaginary frequencies (NIMAG = 0). MO pictures are generated through the GV03[65] viewing software. The ionization potential (I), electron affinity (A), and hardness (η) are calculated using the ΔSCF method. The adiabatic electron affinity in a chemical reaction is calculated using eq 5. Atomic charges and Fukui functions are calculated using both the Mulliken population analysis (MPA)[66] and natural population analysis (NPA)[67] schemes, and only MPA results are reported in all of the cases.

Results and Discussion

Stability, Reactivity, and Aromaticity of All-Metal Be_3^{2-}, MBe_3^-, and M_2Be_3 [M = Li, Na, Cu]. Figure 1 shows the optimized geometries of the possible linear ($D_{\infty h}$) and closed (D_{3h}) isomers of the Be_3^{2-} molecule. Table 1 presents the energy (E), relative energy (Rel. E), polarizability (α), hardness (η), electrophilicity (ω), nucleofugality (ΔE_n) and the ΔX ($X = E$, α, η, ω, ΔE_n) values of the Be_3^{2-} isomers. It is found that cyclic Be_3^{2-} (D_{3h}) is energetically more stable, less polarizable, and harder than the open Be_3^{2-}, that is, $\Delta X < 0$ ($X = E$, α) and > 0 ($X = \eta$), as expected from the principles of minimum energy (MEP), minimum polarizability (MPP), and maximum hardness (MHP), that is, when a conformer changes from the most stable to other less stable species in most cases, the energy increases, the hardness decreases, and the polarizability increases. The delocalization of the electrons and the three body forces[15] in the Be_3^{2-} (D_{3h}) isomer lead to its lower energy compared to its open ($D_{\infty h}$) form. A valence-type bonding with π-in-plane phase character may be expected[15] for the triangular Be_3^{2-}, as was analyzed from the density difference maps in the past.[68] The electrofugality and nucleofugality indices are used to characterize the silica nanostructures[69] and biological systems.[70] It is known that nucleofugality and electrofugality are directly related to the stability of anions and cations, respectively.[62] For the Be_3^{2-} dianion isomers, the energetically more stable D_{3h} isomer possesses more nucleofugality (ΔE_n) compared to that of its open form, that is, $\Delta(\Delta E_n) > 0$, as expected. In order to check the stability of the Be_3^{2-} (D_{3h}), two possible decomposition channels are considered as follows

$$Be_3^{2-}(g) \rightarrow Be_2(g) + Be(g) + 2e^- \tag{14a}$$

$$Be_3^{2-}(g) \rightarrow Be_3^-(g) + e^- \tag{14b}$$

We consider the electrons after dissociation to be free. The energies of the various components in the reactions in eq 14 and the associated ΔE_e values are presented in Table 2. The ΔE_e values obtained in the present work, namely, 0.630(0.450) eV ($Be_2 \rightarrow Be_2^-$), −3.075 eV ($Be_3^- \rightarrow Be_3^{2-}$), and 1.413(1.535) eV ($Be_3 \rightarrow Be_3^-$), match well with those reported in ref 15 calculated at the MP2 level of theory (presented within the parentheses). It is found that the energy of the Be_3^{2-} (D_{3h}) dianion is slightly above compared to its fragments from the decomposition channels (eq 14). Therefore, a metastable nature of this Be_3^{2-} (D_{3h}) unit may be expected. It deserves a careful scrutiny.

Figures 2 and 3 present the minimized geometries of all of the possible stable isomers of the MBe_3^- (M = Li, Na, Cu) and M_2Be_3 (M = Li, Na, Cu) molecules, respectively. Geometrical parameters of the MBe_3^- and M_2Be_3 molecules are

TABLE 2: Adiabatic Electron Affinity (ΔE_e) and Energy (E) of the Be_3^{2-} (D_{3h}) and MBe_3^- [M = Li, Na, Cu] (C_{3v}) along with Their Various Decomposed Forms

ΔE_e (AEA)^a	0.0231 [$Be_2 \rightarrow Be_2^-$]	−0.1130 [$Be_3^- \rightarrow Be_3^{2-}$]	0.0519 [$Be_3 \rightarrow Be_3^-$]
Energy^{a,b}	$E(Be_3^{2-})$	$E(Be_2) + E(Be)$	$E(Be_3^-)$
	−44.0034	−44.0207	−44.1164
Energy^{a,b}	$E(MBe_3^-)$	$E(M) + E(Be_2) + E(Be)$	$E(M) + E(Be_3)$
M = Li	−51.6765	−51.5120	−51.5558
M = Na	−206.4547	−206.3075	−206.3513
M = Cu	−1684.7038	−1684.4930	−1684.5368

[a] In au. [b] Electrons after dissociation are considered to be free.

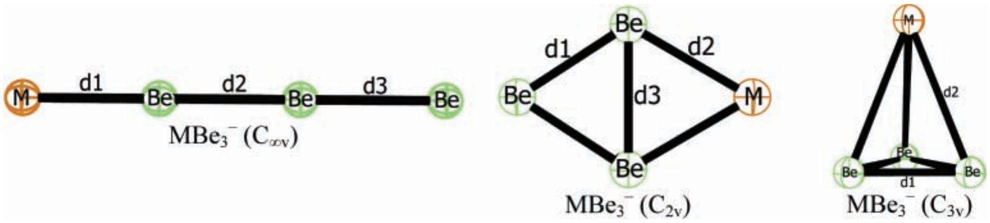

Figure 2. Optimized geometries of the open and closed isomers of MBe_3^- [M = Li, Na, Cu]. Geometrical parameters are provided in Table 3.

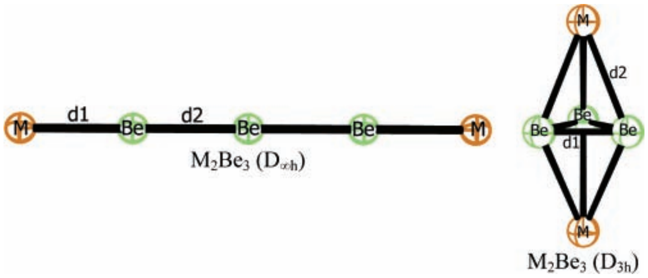

Figure 3. Optimized geometries of the open and closed isomers of M_2Be_3 [M = Li, Na, Cu]. Geometrical parameters are provided in Table 3.

provided in Table 3. Three possible isomers are found for MBe_3^- with $C_{\infty v}$, C_{2v}, and C_{3v} symmetries. Table 4 shows the energy (E), relative energy (Rel. E), polarizability (α), hardness (η), electrophilicity (ω), nucleofugality (ΔE_n), and the ΔX ($X = E, \alpha, \eta, \omega, \Delta E_n$) values of the various isomers of the MBe_3^- (M = Li, Na, Cu) molecule. The C_{3v} isomer of MBe_3^- is found to be the most stable in energy and the hardest, whereas the C_{2v} isomer is found to be the least polarizable. For both the closed system C_{3v} and C_{2v}, it is found that $\Delta X < 0$ for $X = E$, α and > 0 for $X = \eta$, ΔE_n (except for $\Delta\eta$ and $\Delta(\Delta E_n)$ values of $NaBe_3^-$ (C_{2v})), which suggests their stable and possible aromatic nature. The ΔE_n values are more for the energetically more stable closed isomers compared to their related open forms, as expected. It may also be noted that the ΔE_n values for these isomers are $\Delta E_n [C_{3v}] > \Delta E_n [C_{2v}] > \Delta E_n [C_{\infty v}]$, which implies a direct relationship between the stability and the nucleofugality.[62] The stability of the MBe_3^- (C_{3v}) isomer may be investigated through the following decompositions

$$MBe_3^-(g) \rightarrow M(g) + Be_2(g) + Be(g) + e^- \qquad (15a)$$

$$MBe_3^-(g) \rightarrow M(g) + Be_3(g) + e^- \qquad (15b)$$

The electrons after the dissociation are considered to be free. The energies of the respective components in the reactions in eq 15 along with the associated adiabatic electron affinity (ΔE_e) are presented in Table 2. It may be noted that both of the schemes (eq 15a,b) show the stability of these MBe_3^- (C_{3v})

TABLE 3: Geometrical Parameters of the MBe_3^- and M_2Be_3 [M = Li, Na, Cu] Isomers

	MBe_3^- [M = Li, Na, Cu]									M_2Be_3 [M = Li, Na, Cu]					
	$C_{\infty v}$			C_{2v}			C_{3v}			$D_{\infty h}$			D_{3h}		
(Å)	Li	Na	Cu	Li	Na	Cu	Li	Na	Cu	Li	Na	Cu	Li	Na	Cu
$d1$	2.447	2.848	2.129	2.006	1.981	1.957	2.037	2.058	2.083	2.463	2.721	2.077	2.013	2.049	2.168
$d2$	2.032	2.229	2.204	2.371	2.687	2.119	2.487	2.847	2.168	2.160	2.160	2.118	2.478	2.802	2.151
$d3$	2.042	2.274	2.276	2.063	2.104	2.141									

TABLE 4: Relative Energy (ΔE), Relative Polarizability ($\Delta\alpha$), Relative Hardness ($\Delta\eta$), Relative Electrophilicity ($\Delta\omega$), and Relative Nucleofugality (ΔE_n) Values for Various Isomers of MBe_3^-

		closed isomer		open isomer	$\Delta X = X_{Closed} - X_{Open}$ ($X = E, \alpha, \eta, \omega, \Delta E_n$)	
MBe_3^-	X (E,α,η)	MBe_3^- (C_{2v})	MBe_3^- (C_{3v})	MBe_3^- ($C_{\infty v}$)	C_{2v}	C_{3v}
E^a (Rel. E)	$LiBe_3^-$	−51.6457 (0.0308)	−51.6765 (0.0)	−51.6022 (0.0743)	−0.0435	−0.0744
	$NaBe_3^-$	−206.4207 (0.0340)	−206.4547 (0.0)	−206.4025 (0.0522)	−0.0182	−0.0522
	$CuBe_3^-$	−1684.6608 (0.0430)	−1684.7038 (0.0)	−1684.6392 (0.0646)	−0.0216	−0.0646
α^a	$LiBe_3^-$	−200.4670	352.3943	663.3003	−863.7674	−310.9060
	$NaBe_3^-$	308.6333	392.9687	1198.3490	−889.7157	−805.3803
	$CuBe_3^-$	86.9907	245.6043	666.1617	−579.1710	−420.5574
η^b	$LiBe_3^-$	1.2792	1.6423	0.6604	0.6189	0.9819
	$NaBe_3^-$	0.8835	1.6186	1.2776	−0.3941	0.3410
	$CuBe_3^-$	1.6035	2.3235	1.0579	0.5457	1.2656
ω^b	$LiBe_3^-$	0.0946	0.0149	0.0166	0.0780	−0.0017
	$NaBe_3^-$	0.0278	0.0053	0.0162	0.0116	−0.0109
	$CuBe_3^-$	0.0988	0.0012	0.1353	−0.0365	−0.1341
$\Delta E_n{}^b$	$LiBe_3^-$	1.8184	1.8712	0.8167	1.0017	1.0545
	$NaBe_3^-$	1.1191	1.7526	1.4891	−0.3700	0.2635
	$CuBe_3^-$	2.2158	2.3987	1.6606	0.5553	0.7381

[a] In au. [b] In eV.

TABLE 5: Relative Energy (ΔE), Relative Polarizability ($\Delta\alpha$), Relative Hardness ($\Delta\eta$), Relative Electrophilicity ($\Delta\omega$), and Relative Nucleofugality (ΔE_n) Values for Various Isomers of M_2Be_3

M_2Be_3	X (E,α,η)	closed isomer M_2Be_3 (D_{3h})	open isomer M_2Be_3 ($D_{\infty h}$)	$\Delta X = X_{Closed} - X_{Open}$ ($X = E$, α, η, ω, ΔE_n)
E^a (Rel. E)	Li_2Be_3	−59.2040 (0.0)	−59.1446 (0.0594)	−0.0594
	Na_2Be_3	−368.7536 (0.0)	−368.7152 (0.0384)	−0.0384
	Cu_2Be_3	−3325.2176 (0.0)	−3325.1891 (0.0284)	−0.0284
α^a	Li_2Be_3	192.7260	305.8177	−113.0917
	Na_2Be_3	246.8217	350.5893	−103.7676
	Cu_2Be_3	163.6910	162.2363	1.4547
η^b	Li_2Be_3	2.6969	2.0649	0.6320
	Na_2Be_3	2.4609	1.9710	0.4899
	Cu_2Be_3	2.8721	2.8415	0.0306
ω^b	Li_2Be_3	2.4272	1.7193	0.7080
	Na_2Be_3	2.3427	1.8476	0.4951
	Cu_2Be_3	3.0444	2.6048	0.4396
$\Delta E_n{}^b$	Li_2Be_3	0.2922	0.2599	0.0323
	Na_2Be_3	0.2366	0.1961	0.0405
	Cu_2Be_3	0.2125	0.2964	−0.0839

[a] In au. [b] In eV.

TABLE 6: Chemical Hardness (η^a) and Electrophilicity Index (ω^a) Values of the Reactants and Product along with the Reaction Energies ($\Delta E_R = E_p - E_r$) and Heat of Formations (ΔH) of the Reaction Producing the Various Isomers of the MBe_3^- and M_2Be_3 (M = Li, Na, Cu) Molecules

$Li^+ + Be_3^{2-} \rightarrow LiBe_3^-$ (C_{2v})
η: 35.215 0.914 1.279
ω: 23.672 8.702 0.095
$\Delta E_R = -94.6842$ kcal/mol
$\Delta H = -93.7906$ kcal/mol

$Na^+ + Be_3^{2-} \rightarrow NaBe_3^-$ (C_{2v})
η: 21.099 0.914 0.884
ω: 16.667 8.702 0.028
$\Delta E_R = -81.8858$ kcal/mol
$\Delta H = -81.2263$ kcal/mol

$Cu^+ + Be_3^{2-} \rightarrow CuBe_3^-$ (C_{2v})
η: 6.3988 0.914 1.604
ω: 16.284 8.702 0.099
$\Delta E_R = -116.1639$ kcal/mol
$\Delta H = -115.1950$ kcal/mol

$Li^+ + Be_3^{2-} \rightarrow LiBe_3^-$ (C_{3v})
η: 35.215 0.914 1.642
ω: 23.672 8.702 0.015
$\Delta E_R = -114.0369$ kcal/mol
$\Delta H = -113.2030$ kcal/mol

$Na^+ + Be_3^{2-} \rightarrow NaBe_3^-$ (C_{3v})
η: 21.099 0.914 1.619
ω: 16.667 8.702 0.005
$\Delta E_R = -103.1952$ kcal/mol
$\Delta H = -102.6260$ kcal/mol

$Cu^+ + Be_3^{2-} \rightarrow CuBe_3^-$ (C_{3v})
η: 6.3988 0.914 2.324
ω: 16.284 8.702 0.001
$\Delta E_R = -143.1593$ kcal/mol
$\Delta H = -142.4484$ kcal/mol

$2Li^+ + Be_3^{2-} \rightarrow Li_2Be_3$ (D_{3h})
η: 70.430 0.914 2.697
ω: 47.345 8.702 2.427
$\Delta E_R = -136.7681$ kcal/mol
$\Delta H = -135.1499$ kcal/mol

$2Na^+ + Be_3^{2-} \rightarrow Na_2Be_3$ (D_{3h})
η: 42.198 0.914 2.461
ω: 33.333 8.702 2.343
$\Delta E_R = -110.8280$ kcal/mol
$\Delta H = -109.7351$ kcal/mol

$2Cu^+ + Be_3^{2-} \rightarrow Cu_2Be_3$ (D_{3h})
η: 12.798 0.914 2.872
ω: 32.567 8.702 3.044
$\Delta E_R = -169.1865$ kcal/mol
$\Delta H = -167.9134$ kcal/mol

[a] In *e*V.

isomers. For M_2Be_3 molecules, only one closed isomer with D_{3h} symmetry is found to be stable (Figure 3). In this case, also the closed D_{3h} isomer of M_2Be_3 is found to be energetically more stable, less polarizable (except for Cu_2Be_3), and harder compared to its linear ($D_{\infty h}$) counterpart ($\Delta X < 0$ for $X = E$, α; > 0 for $X = \eta$), as expected from the MEP, MPP, and MHP, respectively (Table 5). Table 6 shows the reaction energies of the reactions along with the hardness (η) and electrophilicity (ω) values of the reactants and products to form the energetically most stable isomers of the MBe_3^- and M_2Be_3 molecules. It may be noted that all of the reaction energies to form MBe_3^- and M_2Be_3 are negative, which implies that the reactions are exothermic in nature and therefore thermodynamically favorable.

It may be noted that for all of the reactions, the system with the minimum electrophilicity value lies on the product side, which is expected from the minimum electrophilicity principle (MElP).[41] The MHP does not follow for these reactions, which may be expected due to the presence of strong electrostatic interactions (i.e., charge controlled[71]) among the reactants like Li^+, Na^+, Cu^+, and so forth, which are known to be hard acids, and the MHP is known not to agree with the HSAB principle in most such cases.[71e] Although the MHP can predict the most and the least stable isomers in many cases, it often fails to predict the order of relative stability[72] due to various reasons.[25c,72a−d] For double exchange reactions (apt for understanding the HSAB principle[25c]), the MHP and the MPP perform better[40d] than the MElP. A reverse trend is also observed in some cases.[73] A thorough analysis[41] on this aspect beyond the numerical results is warranted as based on numerical results Zhang and Yang concluded that,[72e] "We should also be cautious of, and suspicious about, using the above ab initio or first-principle methods to calculate and compare energies because these calculated energies have been shown not to be consistently reliable in determining the relative stability of many tautomers"!

Figure 4 presents some of the important frontier molecular orbitals (MOs) of the Be_3^{2-} (D_{3h}) and its species, namely, the MBe_3^- (C_{3v}) and M_2Be_3 (D_{3h}) (M = Li, Na, Cu) molecules. Among the four possible occupied valence orbitals of the Be_3^{2-} (HOMO and HOMO-n, $n = 1-3$), only HOMO and HOMO-1 are shown. The HOMO of Be_3^{2-} is a π-delocalized molecular orbital. The complexes of the Be_3^{2-}, namely, MBe_3^- (C_{3v}) and M_2Be_3 (D_{3h}), show the similar orbital patterns. An antibonding feature may be noted in the LUMOs of all of the respective molecules. The MO pictures of Be_3^{2-} and its species suggest the possible π-aromaticity in these systems, unlike Al_4^{2-} and its various all-metal complexes which possess both the σ and π aromaticities.[3] Also, the cyclic Be_3^{2-} follows the Hückel's $4n + 2$ ($n = 0$) π-electron rule of aromaticity, which is responsible for its greater stability compared to its open ($D_{\infty h}$) form.

Table 7 shows the NICS(0) and NICS(1) values of the Be_3^{2-} (D_{3h}), MBe_3^-, and M_2Be_3 molecules. It is found that NICS(0) values of the Be_3^{2-} unit are large negative values (−65.06 ppm) compared to those of the prototypical aromatic molecule, benzene (−8.89 ppm)[21] and even larger than the recently synthesized all-metal aromatic superatom Al_4^{2-} (−34.42 ppm)[18,21]

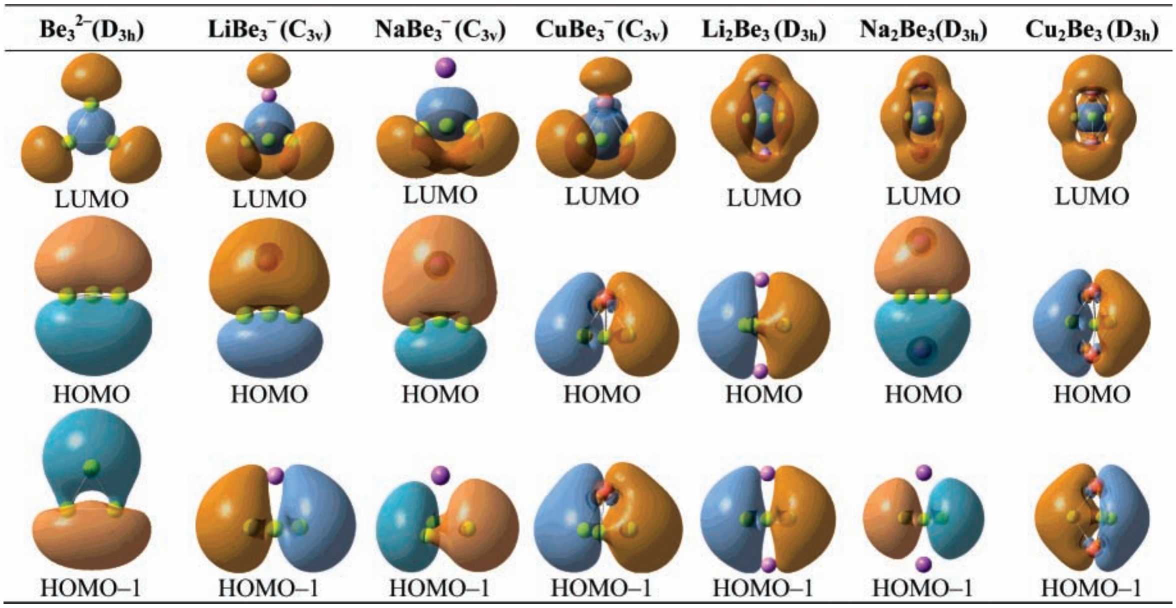

Figure 4. Some important frontier molecular orbital pictures of the Be_3^{2-} (D_{3h}), MBe_3^- (C_{3v}), and M_2Be_3 (D_{3h}) [M = Li, Na, Cu] molecules.

TABLE 7: NICS(0) [NICS(1)][a] Values of the Be_3^{2-} (D_{3h}), MBe_3^- (C_{2v}), MBe_3^- (C_{3v}), and M_2Be_3 (D_{3h}) [M = Li, Na, Cu] Molecules

	MBe_3^- (C_{2v})			MBe_3^- (C_{3v})			M_2Be_3 (D_{3h})		
Be_3^{2-} (D_{3h})	$LiBe_3^-$	$NaBe_3^-$	$CuBe_3^-$	$LiBe_3^-$	$NaBe_3^-$	$CuBe_3^-$	Li_2Be_3	Na_2Be_3	Cu_2Be_3
−65.06 [−31.82]	−49.13 [−25.92]	−52.41 [−27.03]	-54.57 [−26.07]	−38.88 [−32.76]	−35.38 [−35.32]	−43.48 [−89.87]	−42.05 [−25.28]	−45.01 [−28.28]	−47.25 [−90.82]

[a] In ppm.

calculated at the same level of theory. This implies the high aromatic nature of the dianion Be_3^{2-}. Also, high negative NICS values of the different isomers of the MBe_3^- (M = Li, Na, Cu) and M_2Be_3 (M = Li, Na, Cu) molecules show their reasonable aromatic character. It may be noted that the complexation of the Be_3^{2-} unit to its most stable isomers, namely, MBe_3^- (C_{3v}) and M_2Be_3 (D_{3h}), leads to a decrease in aromaticity (Table 7) according to the NICS value, as was found for the aromatic Al_4^{2-} unit during its complexation to form the most stable MAl_4^- (C_{4v}) (M = Li, Na, K, Cu) isomers,[18] although they are found to be energetically and thermodynamically more stable. Also, the planar complexes of Be_3^{2-}, MBe_3^- (C_{2v}) are more aromatic compared to their pyramidal counterparts, MBe_3^- (C_{3v}), as was noticed[17] in the case of the planar MAl_4^- (C_{2v}) when compared to their pyramidal isomers, MAl_4^- (C_{4v}) (M = Li, Na, K, Cu).

The atomic charges are expected to play a major role in understanding the electrostatic interaction.[71] A large negatively (positively) charged species prefers to combine with a positively (negatively) charged species or a hard electrophile (nucleophile). The hard−hard interactions are charged controlled, while the soft−soft interactions are frontier controlled.[71] Table 8 shows the atomic charge and philicity values at each atomic site of the Be_3^{2-} isomers. It may be noted that in the case of the D_{3h} isomer, both the charge (Q_k) and philicity (ω^+, ω^-) values for nucleophilic/electrophilic attack at each beryllium site are almost equal, as expected from its equilateral triangular-planar structure. On the other hand, the charge and philicity values are not equal at each atomic site of the $D_{\infty h}$ isomer, which may be due to the absence of symmetric electron delocalization. Table 9 presents the atomic charges (Q_k) and group philicity (ω_g^+, ω_g^-) values of the Be_3^{2-} nucleophile and the M^+ (M = Li, Na, Cu) electrophile in the MBe_3^- isomers. In the case of MBe_3^- (C_{2v}) isomers, the Be atom opposite to the M (Li, Na, Cu) atoms possesses maximum negative charges (−0.3930, −0.4846, −0.6454) and is therefore the most preferable site for interacting with a hard electrophile. For MBe_3− (C_{3v}) isomers, all of the three Be atoms carry equal negative charges, as expected from their pyramidal symmetry. It is found that in all MBe_3^- isomers, the nucleophilicity of the Be_3^{2-} unit overwhelms its electrophilic trend (i.e., $\omega_g^- > \omega_g^+$), which provides a positive $\Delta\omega_g^{\mp}$ value, as expected. The atomic charges (Q_k) and group philicity (ω_g^+, ω_g^-) values of the Be_3^{2-} and M_2^{2+} (M = Li, Na, Cu, Zn) units in the M_2Be_3 isomers and $[Be_3Zn_2Be_3]^{2-}$ complex are given in Table 10. The electrophilicity (ω) values reported in Tables 8−10 are for the respective molecules, namely, Be_3^{2-}, MBe_3^-, M_2Be_3, and $[Be_3Zn_2Be_3]^{2-}$. For M_2Be_3 ($D_{\infty h}$) isomers, the central Be atom possesses the maximum negative charges (−1.9471, −5.9687, −0.1681) and therefore is the most preferable to attract a positively charged species. In M_2Be_3 (D_{4h}) isomers, the charges on all of the three Be atoms are equally distributed, and a similar

TABLE 8: Atomic Charge (Q_k), Electrophilicity (ω),[a] and Philicity (ω^+, ω^-)[a] Values for Nucleophilic and Electrophilic Attacks, Respectively, for the Beryllium Atoms of Different Isomers of the Be_3^{2-} Unit

isomers	atom	charge (Q_k)	ω	ω^+	ω^-
Be_3^{2-} ($D_{\infty h}$)	Be	−1.5912		18.1792	11.3330
	Be	−0.2044	7.632	−5.2734	−1.8503
	Be	−0.2044		−5.2734	−1.8503
Be_3^{2-} (D_{3h})	Be	−0.6665		2.8999	2.9046
	Be	−0.6665	8.702	2.8999	2.9046
	Be	−0.6670		2.9027	2.8932

[a] In eV.

TABLE 9: Atomic Charge (Q_k), Electrophilicity (ω),[a] and Group Philicity (ω_g^+, ω_g^-)[a] Values for Nucleophilic and Electrophilic Attacks, Respectively, for the Ionic Units of Different Isomers of MBe_3^- [M = Li, Na, Cu]

isomers	atom	charge (Q_k)	ω	unit	ω_g^+	ω_g^-	$\Delta\omega_g^{\mp}$
$LiBe_3^-$	Be	−0.5881, −0.7002, −0.0710	0.0166	Be_3^{2-}	−0.0209	0.0114	0.0323
($C_{\infty v}$)	Li	0.3594		Li^+	0.0375	0.0052	−0.0323
$LiBe_3^-$	Be	−0.3501, −0.3501, −0.3930	0.0946	Be_3^{2-}	−0.0644	0.0534	0.1178
(C_{2v})	Li	0.0931		Li^+	0.159	0.0411	−0.1178
$LiBe_3^-$	Be	−0.4019, −0.4021, −0.4017	0.0149	Be_3^{2-}	−0.0142	0.0105	0.0246
(C_{3v})	Li	0.2056		Li^+	0.0291	0.0045	−0.0246
$NaBe_3^-$	Be	−1.4921, 0.5335, −0.3513	0.0162	Be_3^{2-}	−0.0513	0.0070	0.0583
($C_{\infty v}$)	Na	0.3098		Na^+	0.0675	0.0091	−0.0583
$NaBe_3^-$	Be	−0.3425, −0.3425, −0.4846	0.0278	Be_3^{2-}	−0.0130	0.0181	0.0311
(C_{2v})	Na	0.1696		Na^+	0.0408	0.0097	−0.0311
$NaBe_3^-$	Be	−0.3998, −0.3998, −0.3998	0.0053	Be_3^{2-}	−0.0011	0.0035	0.0047
(C_{3v})	Na	0.1994		Na^+	0.0065	0.0018	−0.0047
$CuBe_3^-$	Be	−1.8161, 0.518, 1.0021	0.1353	Be_3^{2-}	−0.2509	0.0935	0.3444
($C_{\infty v}$)	Cu	−0.7040		Cu^+	0.3862	0.0418	−0.3444
$CuBe_3^-$	Be	0.0273, 0.0273, −0.6454	0.0988	Be_3^{2-}	−0.0428	0.0742	0.1170
(C_{2v})	Cu	−0.4091		Cu^+	0.1416	0.0246	−0.1170
$CuBe_3^-$	Be	−0.1867, −0.1867, −0.1867	0.0012	Be_3^{2-}	−0.0018	0.0009	0.0027
(C_{3v})	Cu	−0.4400		Cu^+	0.0030	0.0003	−0.0027

[a] In eV.

TABLE 10: Atomic Charge (Q_k), Electrophilicity (ω),[a] and Group Philicity (ω_g^+, ω_g^-)[a] Values for Nucleophilic and Electrophilic Attacks, Respectively, for the Ionic Units of Different Isomers of M_2Be_3 [M = Li, Na, Cu] and $[Be_3Zn_2Be_3]^{2-}$

isomers	atom	charge (Q_k)	ω	unit	ω_g^+	ω_g^-	$\Delta\omega_g^{\mp}$
Li_2Be_3	Be	−1.9471, 0.3621, 0.3617	1.7193	Be_3^{2-}	1.2800	0.1568	−1.1232
($D_{\infty h}$)	Li	0.6117, 0.6116		Li_2^{2+}	0.4392	1.5624	1.1232
Li_2Be_3	Be	−0.3483, −0.3483, −0.3483	2.4272	Be_3^{2-}	0.8470	1.6853	0.8383
(D_{3h})	Li	0.5224, 0.5224		Li_2^{2+}	1.5803	0.7419	−0.8383
Na_2Be_3	Be	−5.9687, 2.1025, 2.1044	1.8476	Be_3^{2-}	1.1462	0.5047	−0.6415
($D_{\infty h}$)	Na	0.8808, 0.8811		Na_2^{2+}	0.7014	1.3429	0.6415
Na_2Be_3	Be	−0.3258, −0.3258, −0.3258	2.3427	Be_3^{2-}	0.9382	1.4717	0.5335
(D_{3h})	Na	0.4887, 0.4887		Na_2^{2+}	1.4045	0.8711	−0.5335
Cu_2Be_3	Be	−0.1681, 0.7200, 0.7200	2.6048	Be_3^{2-}	1.1741	0.2273	−0.9468
($D_{\infty h}$)	Cu	−0.6360, −0.6360		Cu_2^{2+}	1.4307	2.3775	0.9468
Cu_2Be_3	Be	0.0983, 0.0983, 0.0983	3.0444	Be_3^{2-}	1.2438	1.6514	0.4076
(D_{3h})	Cu	−0.1474, −0.1474		Cu_2^{2+}	1.8006	1.3930	−0.4076
$[Be_3Zn_2Be_3]^{2-}$	Be	−0.2089, −0.2048, −0.2050 −0.2065, −0.2082, −0.2039	2.2348	$2Be_3^{2-}$	−7.8187	1.0904	8.9091
(D_{3h})	Zn	−0.3812, −0.3814		Zn_2^{2+}	10.054	1.1444	−8.9091

[a] In eV.

situation is found for the two M (Li, Na, Cu) atoms, which is expected from their point group symmetry. Although in the case of the most stable D_{3h} isomers $\Delta\omega_g^{\mp}$ of Be_3^{2-} provides an expected positive value due to its nucleophilic nature, it behaves like an electrophile in the linear $D_{\infty h}$ isomer of M_2Be_3 in both the MPA and NPA calculations. The Li and Na atoms in the MBe_3^- and M_2Be_3 species behave as hard electrophiles (with positive charges), and the Cu atom behaves like a hard nucleophile (with a negative charge). For the most stable C_{3v} isomer of MBe_3^- and D_{3h} isomer of M_2Be_3, the order of $\Delta\omega_g^{\mp}$ for Be_3^{2-} is Li > Na > Cu, which suggests the preference of Li−Be bimetallic species as a better molecular cathode.

Stabilization of the Direct Zn−Zn Bond by the Dianion Be_3^{2-} Superatom. Among the group 12 elements (zinc, cadmium, and mercury), only mercury is well-known for its +1 oxidation state, whereas the other two light elements, cadmium and zinc, possess a +2 oxidation state.[42] Some exceptions are known, for example, dication Cd_2^{2+} has been characterized by X-ray methods[43a] in $Cd_2(AlCl_4)_2$ and by cadmium NMR[43b] in $Cd_2(T_p^{Me2})_2$ (T_p^{Me2} is hydrotris(3,5-dimethylpyrazolyl) borate), there has been formation of Zn_2^{2+} ions in $ZnCl_2$/Zn glasses at high temperatures[44] and in zeolite matrices,[45] and so forth. Resa et al.[46] unexpectedly succeeded to stabilize the direct Zn−Zn bond for the first time by Cp*-(Me_5C_5) to synthesize a compound, decamethyldizincocene, (η^5-$Me_5C_5)_2Zn_2$, which is isolated through the reaction between (η^5-$Me_5C_5)_2Zn$ and Et_2Zn. Cp($C_5H_5^-$) is a well-known unit for sandwiching metal atoms.[74] We consider here a Me-unsubstituted (η^5-$C_5H_5)_2Zn_2$ molecule for our calculation to check whether the following reaction is thermodynamically favorable[47a] (**A**)

$$\text{CpZnCp} + \text{Zn} \rightarrow \text{CpZnZnCp} \quad \Delta H = -18.997 \text{ kcal/mol} \quad (A)$$

We also investigate whether the Be_3^{2-} unit can stabilize the direct Zn−Zn bond by forming a new all-metal compound, $[Be_3ZnZnBe_3]^{2-}$, through the following reaction (**B**)

$$2Zn^+ + 2Be_3^{2-} \rightarrow [Be_3ZnZnBe_3]^{2-} \quad \Delta H = -611.404 \text{ kcal/mol} \quad (B)$$

It is found that the reaction (**B**) producing $[Be_3ZnZnBe_3]^{2-}$(ΔH = −611.404 kcal/mol) is highly exothermic in comparison to the reaction (**A**) to form CpZnZnCp (ΔH = −18.997 kcal/mol).

Figures 5 and 6 show the energy-minimized geometries of the Cp (D_{5h}), CpZnCp (C_S), CpZnZnCp (D_{5h}), and $[Be_3ZnZnBe_3]^{2-}$ (D_{3h}) molecules. The Be_3^{2-} unit in the $[Be_3ZnZnBe_3]^{2-}$ is found

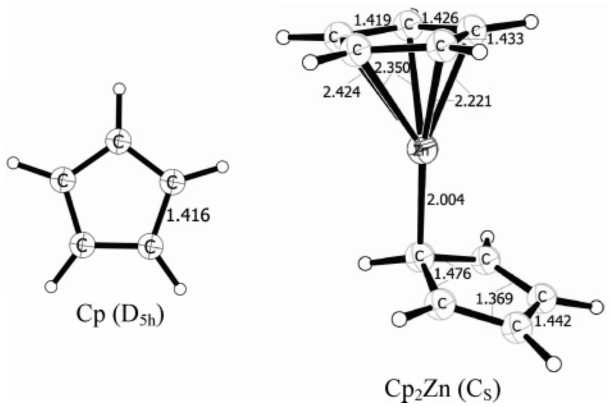

Figure 5. Optimized geometries of the Cp ($C_5H_5^-$) and Cp_2Zn molecules.

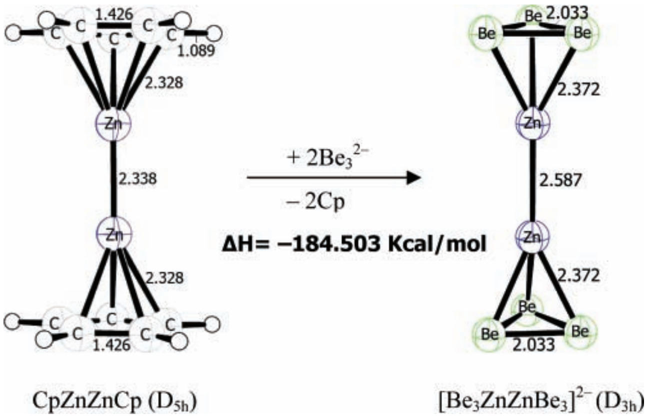

Figure 6. Substitution reaction in CpZnZnCp by Be_3^{2-} to produce $[Be_3ZnZnBe_3]^{2-}$.

to be more aromatic in nature (NICS(0) = −37.00 ppm, NICS(1) = −19.54 ppm) compared to the Cp($C_5H_5^-$) units in CpZnZnCp (NICS(0) = −14.76 ppm, NICS(1) = −10.08 ppm). The sandwiching of Be_3^{2-} into $[Be_3ZnZnBe_3]^{2-}$ shows a decrease of aromatic nature in that unit, whereas for the sandwich complex of Al_4^{2-} {NICS(0) = −34.42 ppm} viz., $M_2(Al_4TiAl_4)$ {NICS(0) = −36.925, −39.736, and −39.456 ppm, respectively, for M = Li, Na and K}, the aromatic nature of that unit increases a bit.[18]

Figure 7 shows some of the important molecular orbital pictures of the Cp (D_{5h}), CpZnZnCp (D_{5h}), and $[Be_3ZnZnBe_3]^{2-}$ (D_{3h}) molecules. Although the HOMO-2 (not shown here) of Cp ($C_5H_5^-$) exhibits π-delocalization, the rest of the MOs of Cp do not show a clear-cut π-character. However, in the HOMO of $[Be_3ZnZnBe_3]^{2-}$, π-delocalization on the Be_3^{2-} units implies the aromaticity as well as the high stability of that molecule.

Finally, Figure 6 shows the substitution reaction

$$C_5H_5ZnZnC_5H_5 + 2Be_3^{2-} \rightarrow [Be_3ZnZnBe_3]^{2-} + 2C_5H_5^- \qquad \Delta H = -184.503 \text{ kcal/mol} \quad (C)$$

It is found that the substitution of Cp ($C_5H_5^-$) units by Be_3^{2-} units provides a highly exothermic reaction ($\Delta H = -184.503$ kcal/mol), which implies the relative stability of the $[Be_3ZnZnBe_3]^{2-}$ molecule.

The distribution of charges on the Be atoms (and also on the Zn atoms) is almost symmetric due to the symmetry of the $[Be_3ZnZnBe_3]^{2-}$. The positive $\Delta\omega_g^{\mp}$ value for Be_3^{2-} in $[Be_3ZnZnBe_3]^{2-}$ is found to be quantitatively large, predicting the highly nucleophilic nature of that unit in the complex.

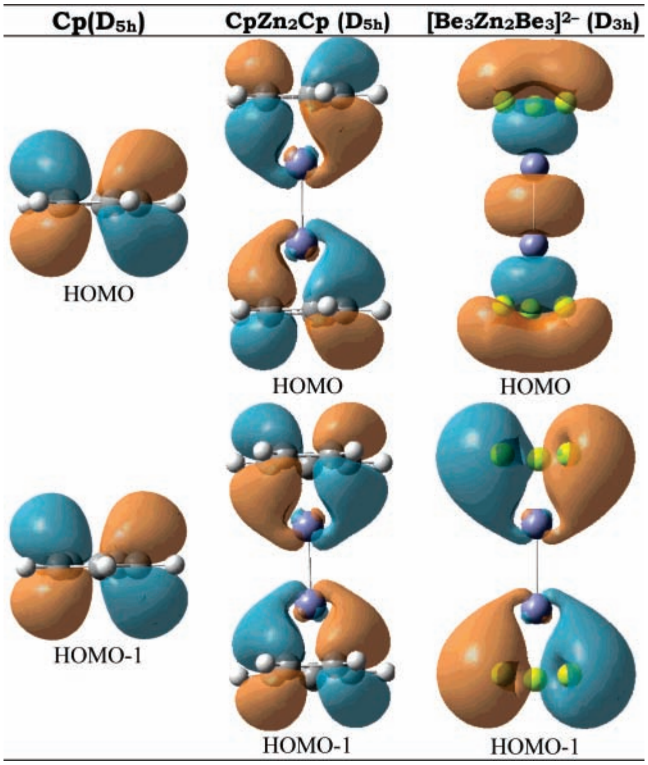

Figure 7. Some important molecular orbital pictures of Cp (D_{5h}), $CpZn_2Cp$ (D_{5h}), and $[Be_3Zn_2Be_3]^{2-}$ (D_{3h}).

Conclusion

All possible stable structures of the Be_3^{2-} dianion and its bimetallic species MBe_3^- and M_2Be_3 [M = Li, Na, Cu] are predicted. It is found that the bimetallic complexes of the Be_3^{2-} unit are thermodynamically stable. The aromaticity of these compounds is predicted in light of the DFT-based descriptors, namely, polarizability (α), hardness (η), and electrophilicity (ω), as well as the well-known magnetic criterion of aromaticity, nucleus-independent chemical shift (NICS). All of the molecules are found to be highly π-aromatic in nature. The direct Zn−Zn bond is stabilized by the Be_3^{2-} superatom, and the corresponding reaction is found to be thermodynamically favorable. The substitution reaction of the Cp($C_5H_5^-$) units in the $Zn_2(\eta^5\text{-}C_5H_5)_2$ compound by the Be_3^{2-} units is also found to be highly exothermic in nature, implying the high stability of this new all-metal compound $[Be_3ZnZnBe_3]^{2-}$ (D_{3h}). The atomic charges on the Be atoms reflect the selectivity of the Be_3^{2-} unit when it interacts with other species. The positive nucleophilic excess ($\Delta\omega_g^{\mp}$) values of the Be_3^{2-} unit in most of the cases imply the applicability of those all-metallic clusters in the field of molecular electronics.

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