

A Non-Nuclear Attractor-Mediated $3c-2e$ σ -Aromatic Core in Triberyllium Hexaoxide

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Abstract: Low-valent main-group clusters that activate small molecules represent an intriguing frontier in modern coordination and cluster chemistry. Herein, the structural topology, correlated electronic structure, excited states, and real-space chemical bonding of the cyclic triberyllium hexaoxide complex $\text{Be}_3(\text{O}_2)_3$ are investigated using meta-GGA density functional theory (TPSS), domain-based local pair natural orbital coupled-cluster theory [DLPNO-CCSD(T)], local energy decomposition (LED), similarity transformed equation-of-motion coupled-cluster theory (STEOM-DLPNO-CCSD), and the Quantum Theory of Atoms in Molecules (QTAIM). The cluster features an equilateral triangular Be_3 core ($d(\text{Be}-\text{Be}) = 2.103\text{--}2.105$ Å) coordinated radially to three end-on dioxygen units ($d(\text{O}-\text{O}) = 1.297$ Å). High-level DLPNO-CCSD(T)/def2-TZVP benchmarks establish a correlation energy of -1.751222 Eh and a total electronic energy of -494.527653 Eh. Extended transition state natural orbitals for chemical valence (ETS-NOCV) analysis reveals that core-to-ligand assembly is driven by strong orbital stabilization ($\Delta E_{\text{orb}} = -503.51$ kcal/mol) overcoming Pauli steric repulsion ($\Delta E_{\text{Pauli}} = +767.52$ kcal/mol), mediated by dative charge flow into the dioxygen π^* manifold. Topological gradient vector field analysis demonstrates that the Be_3 ring lacks classical pairwise Be–Be bond critical points; instead, gradient trajectories converge into a central Non-Nuclear Attractor (NNA) at the ring centroid. Real-space electron localization function (ELF), localized orbital locator (LOL), source function integrations, and delocalization indices ($\Sigma \delta(\text{Be}, \text{Bq}) = 0.971$ e) confirm that the Be_3 core is sustained by a central three-center two-electron ($3c-2e$) σ -aromatic bond.

Keywords: Beryllium Clusters, Multicenter Bonding, Non-Nuclear Attractor, σ -Aromaticity, Dioxygen Activation, QTAIM, DLPNO-CCSD(T).

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I. INTRODUCTION

The formation and stabilization of homometallic bonds among alkaline-earth metals continue to challenge classical bonding paradigms. Beryllium, possessing a compact $1s^2 2s^2$ ground-state configuration and low core-electron count, exhibits substantial covalent character compared to heavier alkaline-earth metals. Small beryllium clusters frequently display non-classical multicenter bonding due to high kinetic stabilization and diffuse s–p hybridization.^{28–40}

When coordinated to oxidizing substrates such as molecular oxygen (O_2), low-valent main-group frameworks undergo cooperative multi-electron transfer. Resolving the resulting electronic structures requires accurate treatment of dynamic correlation alongside real-space topological methods. Herein, we examine $\text{Be}_3(\text{O}_2)_3$, characterizing the interplay between metal–metal multicenter bonding, non-nuclear attractors, and small-molecule activation.

II. COMPUTATIONAL METHODS

Electronic structure calculations were performed using the ORCA 6.1 program package.⁸ Geometry optimizations were conducted with the TPSS meta-GGA functional¹ paired with the def2-TZVP basis set¹⁵ and the def2/J auxiliary Coulomb fitting basis¹⁶ under the Split-RI-J approximation. Single-point electronic ground-state benchmarks and local energy decompositions (LED)^{4,18} were performed using domain-based local pair natural orbital coupled-cluster theory with perturbative triples [DLPNO-CCSD(T)],^{2,17} employing the def2-TZVP/C correlation auxiliary basis¹⁹ and the RIJCOSX approximation²⁰ with VeryTightSCF and TightPNO settings. Natural localized molecular orbitals (NLMOs) were generated via the Foster–Boys localization scheme.²¹

Excited-state electronic structures were evaluated using similarity transformed equation-of-motion coupled-cluster theory (STEOM-DLPNO-CCSD).^{3,22,23} Active spaces were constructed from state-averaged natural orbitals derived from

configuration interaction singles (CIS) spanning six roots. Energy decomposition analysis was executed via the extended transition state method with natural orbitals for chemical valence (ETS-NOCV)^{13,24} under two fragmentation schemes: (i) inter-ring fragmentation separating monomeric BeO₂ from Be₂(O₂)₂, and (ii) core–ligand fragmentation separating the metallic Be₃ ring from the (O₂)₃ ligand shell.

Real-space topological analyses, critical point trajectories, delocalization indices (DI),²⁵ atomic localization indices (LI), source function basin integrations,¹⁴ and Interaction Region Indicator (IRI) isosurfaces²⁶ were

computed using the Multiwfn package.⁶ Topological completeness was verified through the Poincaré–Hopf relationship.^{7,27}

III. RESULTS AND DISCUSSION

► Equilibrium Structure and Correlated Ground-State Benchmark

The optimized structure of Be₃(O₂)₃ exhibits a planar, equilateral triangular Be₃ ring (D_{3h} symmetry) coordinated radially to three end-on dioxygen ligands.

Table 1 Selected Structural Metrics and Calculated Ground-State Properties for Be₃(O₂)₃

Parameter	TPSS/def2-TZVP	DLPNO-CCSD(T)/def2-TZVP
d(Be–Be) (Å)	2.101–2.108	2.103–2.105
d(Be–Oprox) (Å)	1.388–1.389	1.388–1.389
d(O–O) (Å)	1.296–1.298	1.297
∠(Be–Be–Be) (deg)	59.9–60.2	59.98
∠(Be–O–O) (deg)	178.6–179.8	178.6–179.8
E _{tot} (E _h)	–495.529947	–494.527653
E _{corr} (E _h)	---	–1.751222
T ₁ diagnostic	---	0.0264
Dipole Moment, μ (Debye)	0.0181	0.0140
Rotational Constants (MHz)	925.73, 920.02, 461.43	925.73, 920.02, 461.43
Zero-Point Energy, ZPE (kcal/mol)	14.33	
Thermal Enthalpy, H_{298} (E _h)	495.494025	
Entropy Term, $-T\Delta S_{298}$ (kcal/mol)	32.60	
Gibbs Free Energy, G_{298} (E _h)	495.545980	

The Be–Be internuclear distances of 2.103–2.105 Å fall within the range expected for alkaline-earth metal–metal single bonds.¹⁰ The peripheral O–O distances (1.297 Å) are substantially elongated relative to neutral gaseous O₂ (1.207 Å), indicating formal reduction toward superoxo units (~1.28 Å). The computed rotational constants establish an oblate symmetric top ($BA \approx BB \approx 2BC$), confirming a planar geometry. High-level DLPNO-CCSD(T) calculations yield a correlation energy of –1.751222 E_h and a T₁ diagnostic of 0.0264, reflecting modest multireference character within the coordinating oxygen shell.

The peripheral dioxygen units exhibit fundamental stretching frequencies at 1406.40 – 1406.96 cm^{–1} (modes 24 and 25), accompanied by high infrared intensities exceeding 505 km/mol. Mode 26 corresponds to the in-phase symmetric breathing of all three dioxygen ligands at 1441.16 cm^{–1} (0.07 km/mol, active exclusively in Raman scattering). The redshift relative to free O₂ (1580 cm^{–1}) combined with the higher frequency compared to peroxo species (800 – 900 cm^{–1}) provides spectroscopic evidence for superoxide-like activation, matching the calculated Mayer bond order ($B(\text{O–O}) = 0.998$) and QTAIM delocalization index ($\delta(\text{O}, \text{O}) = 1.543$). The radial Be–O framework vibrates at 985.19 – 1076.33 cm^{–1} (modes 21–23), while intermetallic ring vibrations emerge below 372 cm^{–1}.

Thermochemical analysis under standard conditions (298.15 K, 1.00 atm) yields a zero-point vibrational energy (ZPE) of 14.33 kcal/mol (0.022831 E_h) and an overall thermal enthalpy of $H_{298} = -495.494025$ E_h. Applying Grimme's quasi-RRHO model for low-lying vibrational modes provides an entropic stabilization term of $-T\Delta S_{298} = -32.60$ kcal/mol (–0.051956 E_h), yielding a Gibbs free energy of $G_{298} = -495.545980$ E_h.

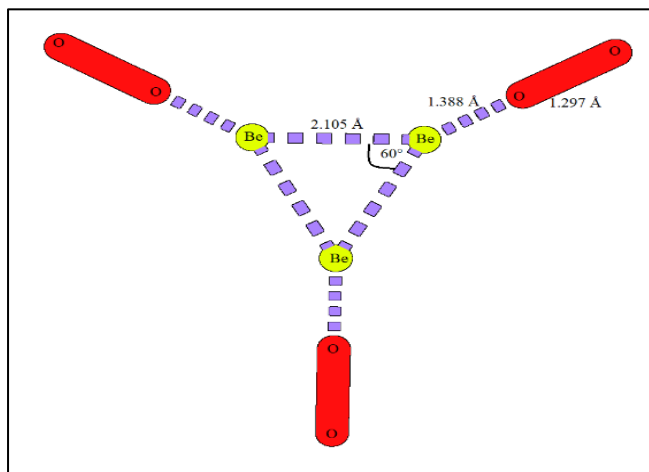


Fig 1 Optimized D_{3h} Equilibrium Geometry (TPSS/def2-TZVP) Showing Key Interatomic Distances: Be–Be = 2.105 Å, Be–Oprox = 1.388 Å, Oprox–Odistal = 1.297 Å.

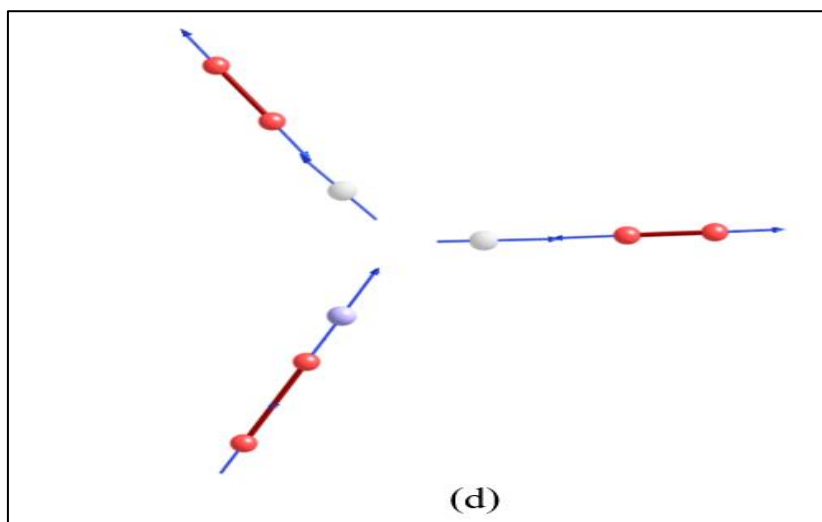
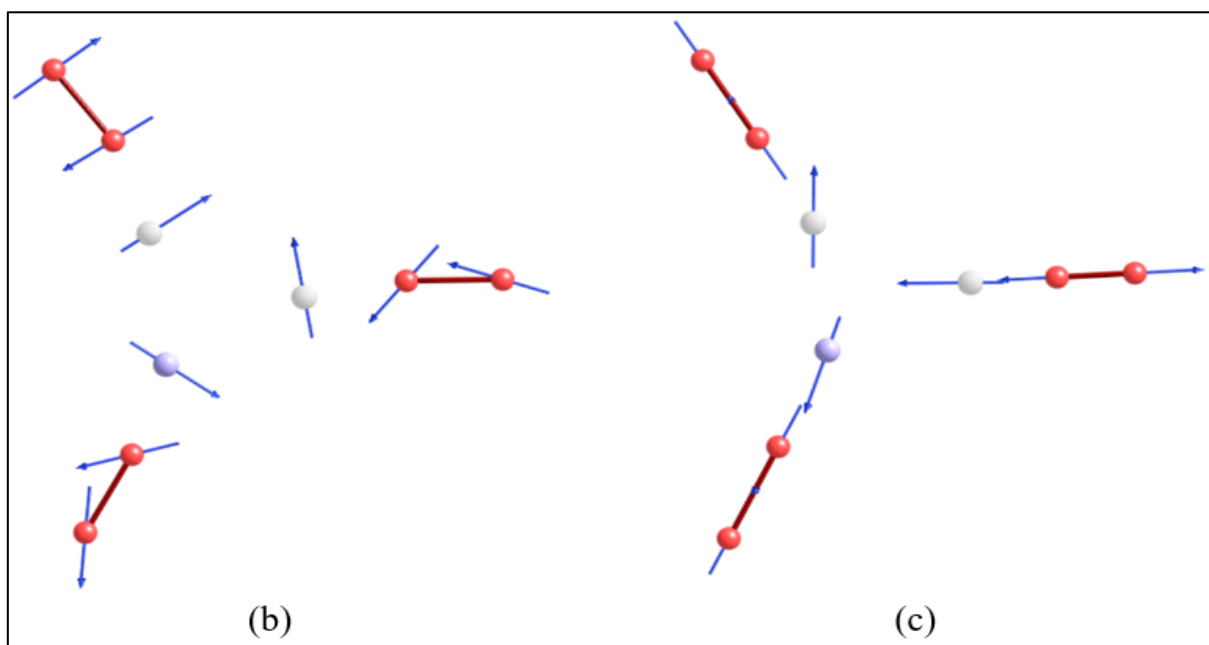
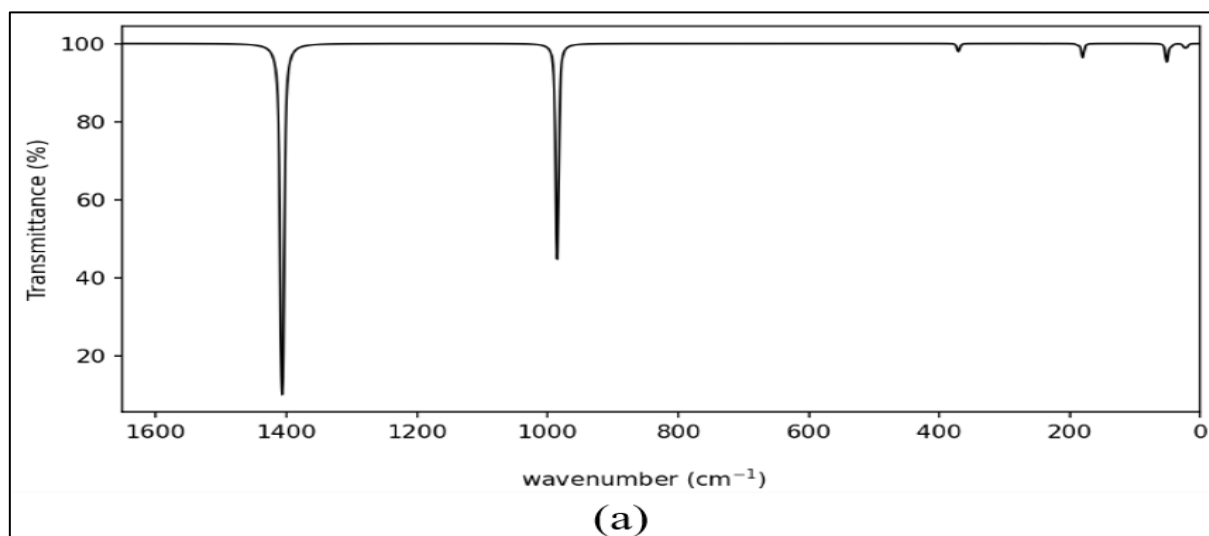


Fig 2 (a) IR Spectrum (b) and (c) Selected Diagnostic Infrared Normal Modes: Asymmetric Be–O Stretch ($\approx 1124 \text{ cm}^{-1}$) and (d) Asymmetric O–O Stretch ($\approx 1387 \text{ cm}^{-1}$), with Displacement Vectors Overlaid. Intensities and Symmetry Labels are given in the Supporting Information.

➤ Local Energy Decomposition (LED) and ETS-NOCV Analyses

To quantify the driving forces stabilizing $\text{Be}_3(\text{O}_2)_3$, local energy decomposition (LED) and ETS-NOCV were performed under two distinct fragmentation protocols.

Table 2 Interaction Energy Decomposition Components for $\text{Be}_3(\text{O}_2)_3$ (in kcal mol^{-1})

Interaction Component	LED Scheme: $[\text{BeO}_2] \cdots [\text{Be}_2(\text{O}_2)_2]$	ETS-NOCV Scheme: $[\text{Be}_3] \cdots [(\text{O}_2)_3]$
Pauli Repulsion (ΔE_{Pauli})	---	+767.52
Electrostatic (ΔE_{elstat})	-2386.60	-237.33
Exchange (ΔE_{exch})	-300.33	-191.45
Orbital Interaction (ΔE_{orb})	---	-503.51
Inter-fragment Correlation (ΔE_{corr})	-91.93	---
Strong Pairs Contribution	-71.84	---
Triples Correction	-19.67	---
Dispersion Contribution	-9.77	---
Total Interaction Energy (ΔE_{int})	-2778.86	-164.71

Table 3 Leading NOCV Deformation Channels for the $\text{Be}_3 \cdots (\text{O}_2)_3$ Binding Interaction

NOCV Channel	$ \nu_k $ (e)	$\Delta E_{\text{orb},k}$ (kcal mol^{-1})	ΔT_k (kcal mol^{-1})	ΔV_k (kcal mol^{-1})
α -NOCV Pair 1	0.9886	-103.08	+375.02	-478.10
β -NOCV Pair 1	0.9649	-73.68	+465.79	-539.46
α -NOCV Pair 3	0.3768	-71.55	+306.13	-377.68
α -NOCV Pair 2	0.7003	-66.03	+221.81	-287.85
β -NOCV Pair 2	0.8900	-60.98	+516.45	-577.43
β -NOCV Pair 3	0.6685	-45.88	+376.21	-422.09

LED analysis across the inter-ring interface reveals strong electrostatic stabilization ($\Delta E_{\text{elstat}} = -2386.60$ kcal/mol) supported by exchange forces ($\Delta E_{\text{exch}} = -300.33$ kcal/mol) and dynamical correlation ($\Delta E_{\text{corr}} = -91.93$ kcal/mol). In the core–ligand ETS-NOCV model, binding between the central Be_3 cycle and the $(\text{O}_2)_3$ shell is driven by orbital interactions ($\Delta E_{\text{orb}} = -503.51$ kcal/mol), which account for 53.9% of the total attractive stabilization and

overcome Pauli repulsion (+767.52 kcal/mol). Decomposition into pairwise NOCV deformation channels identifies α -NOCV Pair 1 ($\Delta E_{\text{orb}} = -103.08$ kcal/mol) and β -NOCV Pair 1 ($\Delta E_{\text{orb}} = -73.68$ kcal/mol) as primary contributors, representing charge transfer from the beryllium 2s/2p framework into the π^* antibonding orbitals of the dioxygen ligands.

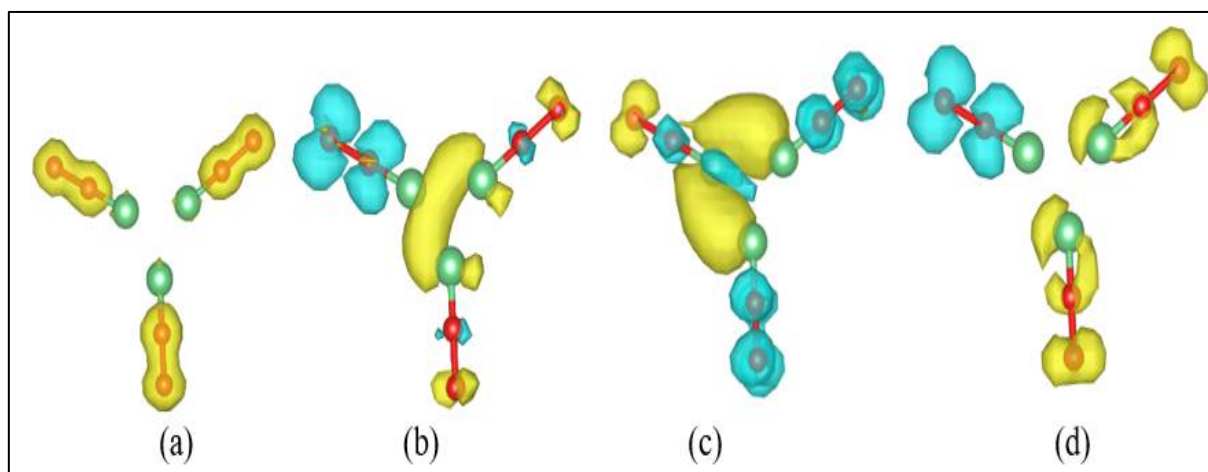


Fig 3 NOCV deformation densities ($\Delta\rho$) illustrating the key bonding and polarization mechanisms during the assembly of $\text{Be}_3(\text{O}_2)_3$. (a) α -NOCV Pair 2 ($\Delta E_{\text{orb}}^{\alpha,2} = -115.75$ kcal/mol), showing concurrent charge accumulation (yellow) into the peripheral $\text{O}_2(\pi^*)$ manifold. (b) α -NOCV Pair 1 ($\Delta E_{\text{orb}}^{\alpha,1} = -15.12$ kcal/mol), highlighting the inter-fragment polarization channel. (c) α -NOCV Pair 4 ($\Delta E_{\text{orb}}^{\alpha,4} = -17.04$ kcal/mol), depicting direct in-plane density flow into the central three-center interstitial bonding region. (d) β -NOCV Pair 1 ($\Delta E_{\text{orb}}^{\beta,1} = +25.75$ kcal/mol), capturing spin-density relaxation during singlet recombination. (Yellow = accumulation, cyan = depletion; isovalue = 0.003 a.u.).

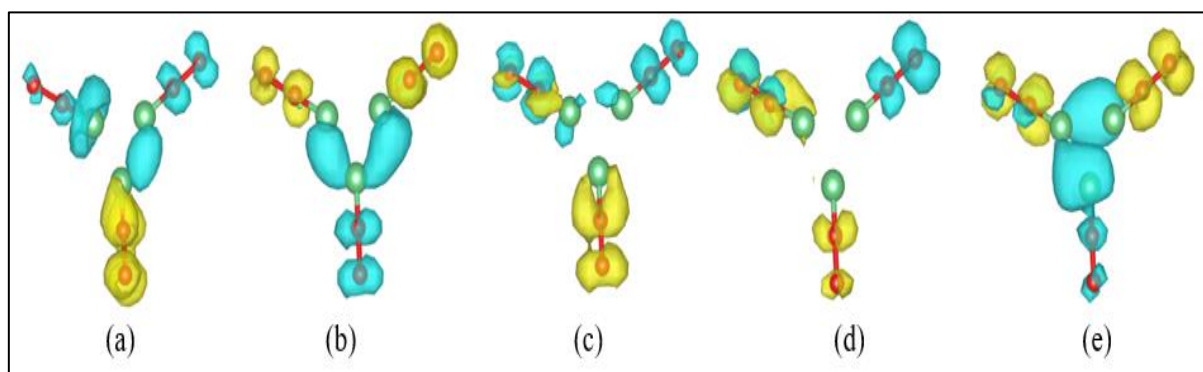


Fig 4 3D NOCV deformation density isosurfaces ($\Delta\rho$) for the core–ligand assembly $[\text{Be}_3] + [(\text{O}_2)_3] \rightarrow \text{Be}_3(\text{O}_2)_3$ (EDA1). (a) α -NOCV Pair 1 ($\Delta E_{\text{orb}}^{\alpha,1} = -103.08$ kcal/mol), showing primary α -spin metal-to-ligand dative transfer. (b) β -NOCV Pair 1 ($\Delta E_{\text{orb}}^{\beta,1} = -73.68$ kcal/mol), illustrating symmetric evacuation of β -density from the Be_3 core into the terminal O_2 shell. (c) α -NOCV Pair 3 ($\Delta E_{\text{orb}}^{\alpha,3} = -71.55$ kcal/mol), depicting radial in-plane π -back-bonding. (d) α -NOCV Pair 2 ($\Delta E_{\text{orb}}^{\alpha,2} = -66.03$ kcal/mol), highlighting in-plane Coulombic polarization. (e) β -NOCV Pair 2 ($\Delta E_{\text{orb}}^{\beta,2} = -60.98$ kcal/mol), reinforcing cooperative β -spin pairing. (Yellow = density accumulation, cyan = density depletion; isovalue = 0.003 a.u.).

➤ Excited-State Transitions and Electronic Instabilities

The low-lying singlet electronic transitions were evaluated using STEOM-DLPNO-CCSD.

Table 4 Low-Lying Singlet Transitions Calculated by STEOM-DLPNO-CCSD

State	Energy (eV)	λ (nm)	fosc (length)	fosc (velocity)	Leading Orbital Character
1 ^1A	−0.366	---	−0.0329	−0.5835	29→30 (70.2%), 28→32 (41.2%)
2 ^1A	−0.356	---	−0.0319	−0.6085	28→30 (69.9%), 29→32 (42.1%)
3 ^1A	+0.570	2175.3	9.36×10^{-7}	1.63×10^{-5}	27→30 (95.3%)
4 ^1A	+0.572	2166.5	2.13×10^{-6}	3.24×10^{-5}	26→30 (95.4%)
5 ^1A	+0.809	1532.4	2.69×10^{-6}	2.12×10^{-5}	25→30 (95.9%)
6 ^1A	+2.313	536.0	1.39×10^{-5}	1.11×10^{-5}	28→31

The lowest vertical singlet transitions yield negative excitation energies (−0.366 and −0.356 eV), indicating that the closed-shell single-reference determinant resides on an electronic instability surface. These states display elevated dipole moments ($|\mu| \approx 5.98\text{--}6.00$ D) relative to the ground state (0.015 D), indicating charge separation into the terminal oxygen atoms. Correlated density evaluations corroborate this picture, showing Mayer free valences of $\text{FA} = 0.720$ on the terminal oxygens, consistent with radicaloid character.

➤ Real-Space Topological Analysis: The Non-Nuclear Attractor σ -Bond

Topological gradient vector field analysis of the electron density $\rho(\mathbf{r})$ reveals 10 attractors (3,−3) and 9 bond critical points (3,−1), satisfying the Poincaré–Hopf relation ($10 - 9 + 0 - 0 = 1$).

Table 5 QTAIM Critical Points, Gradient Paths, and Basin Integration Parameters in $\text{Be}_3(\text{O}_2)_3$

CP Index	Type	Assignment	Connected Path Length	Basin Volume ($\rho > 0.001$ a.u.)	Source Function (a.u.)
CP 1	(3,−3)	Nucleus: O(7) [term]	---	118.19 Bohr ³	0.00369
CP 2	(3,−3)	Nucleus: O(6) [prox]	---	130.58 Bohr ³	0.00409
CP 3	(3,−3)	Nucleus: Be(3)	---	46.99 Bohr ³	0.01385
CP 4	(3,−3)	NNA (Bq, Centroid)	---	109.90 Bohr ³	0.02378
CP 5	(3,−3)	Nucleus: Be(1)	---	47.07 Bohr ³	0.00238
CP 6	(3,−3)	Nucleus: Be(2)	---	47.06 Bohr ³	0.00239
CP 7	(3,−3)	Nucleus: O(8) [prox]	---	130.59 Bohr ³	0.00089
CP 8	(3,−3)	Nucleus: O(9) [term]	---	118.21 Bohr ³	0.00231
CP 9	(3,−3)	Nucleus: O(4) [prox]	---	130.63 Bohr ³	0.00086
CP 10	(3,−3)	Nucleus: O(5) [term]	---	118.20 Bohr ³	0.00232
CP 11	(3,−1)	BCP: O(6)–O(7)	2.451 Bohr	---	---
CP 12	(3,−1)	BCP: Be(3)–O(6)	2.624 Bohr	---	---
CP 13	(3,−1)	BCP: Be(3)–Bq	2.290 Bohr	---	---
CP 14	(3,−1)	BCP: Be(1)–Bq	2.306 Bohr	---	---
CP 15	(3,−1)	BCP: Be(2)–Bq	2.297 Bohr	---	---

CP 16	(3,−1)	BCP: Be(1)–O(8)	2.624 Bohr	---	---
CP 17	(3,−1)	BCP: Be(2)–O(4)	2.624 Bohr	---	---
CP 18	(3,−1)	BCP: O(8)–O(9)	2.451 Bohr	---	---
CP 19	(3,−1)	BCP: O(4)–O(5)	2.451 Bohr	---	---

Table 6 QTAIM Delocalization Indices $\delta(A,B)$ and Localization Indices $\lambda(A)$

Atom/Basin Pair	Interaction Type	Delocalization Index, $\delta(A,B)$
Oprox–Oterm	Intra-dioxygen covalent sharing	1.543
Be–Oprox	Metal–oxygen coordination	0.448–0.449
Be–Be	Direct pairwise metal–metal sharing	0.075–0.076
Be–Bq (centroid)	Multicenter metal–attractor delocalization	0.323–0.324
Sum $\Sigma \delta(Be_i, Bq)$	Total central multicenter delocalization	0.9707 $\approx$ 1.0 pair
Basin Localization (λ)	Be: 2.040 e; Oprox: 7.550 e; Oterm: 6.985 e; Bq: 0.640 e	---

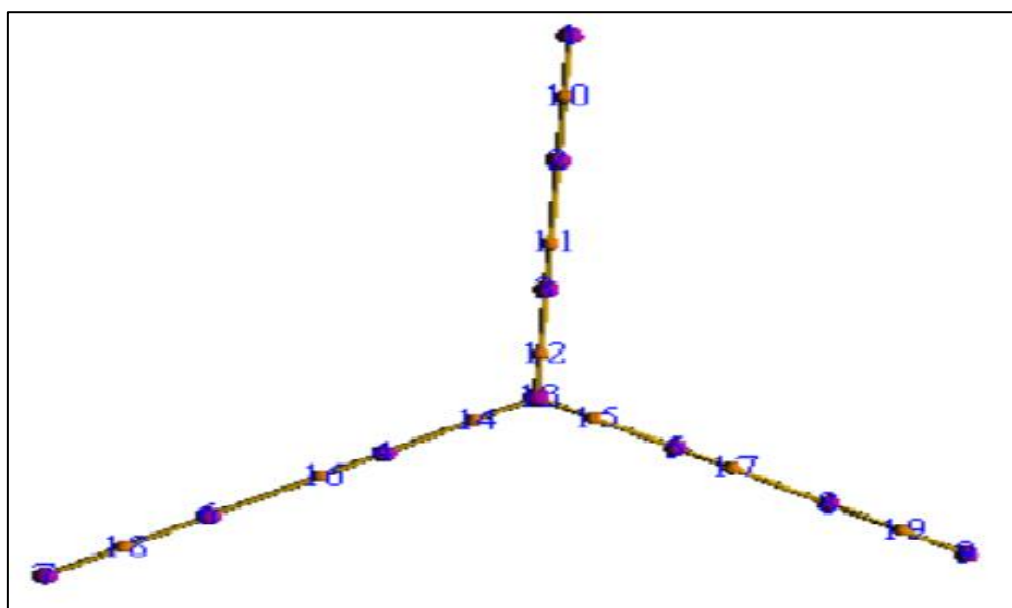


Fig 5 Topological gradient trajectories and critical points of $Be_3(O_2)_3$. Molecular graph illustrating the positions of (3,−3) nuclear attractors (purple), the central non-nuclear attractor (Bq, CP 4), and (3,−1) bond critical points (orange). Bond paths run radially inward from the beryllium nuclei to the central NNA, demonstrating the absence of direct pairwise Be–Be bond paths.

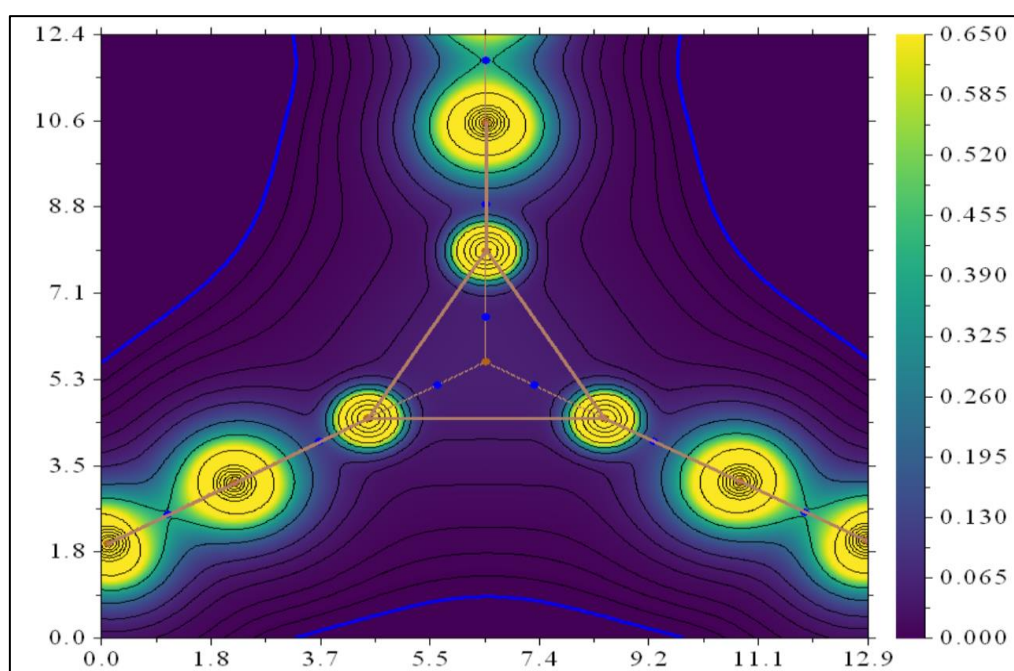


Fig 6 (a)

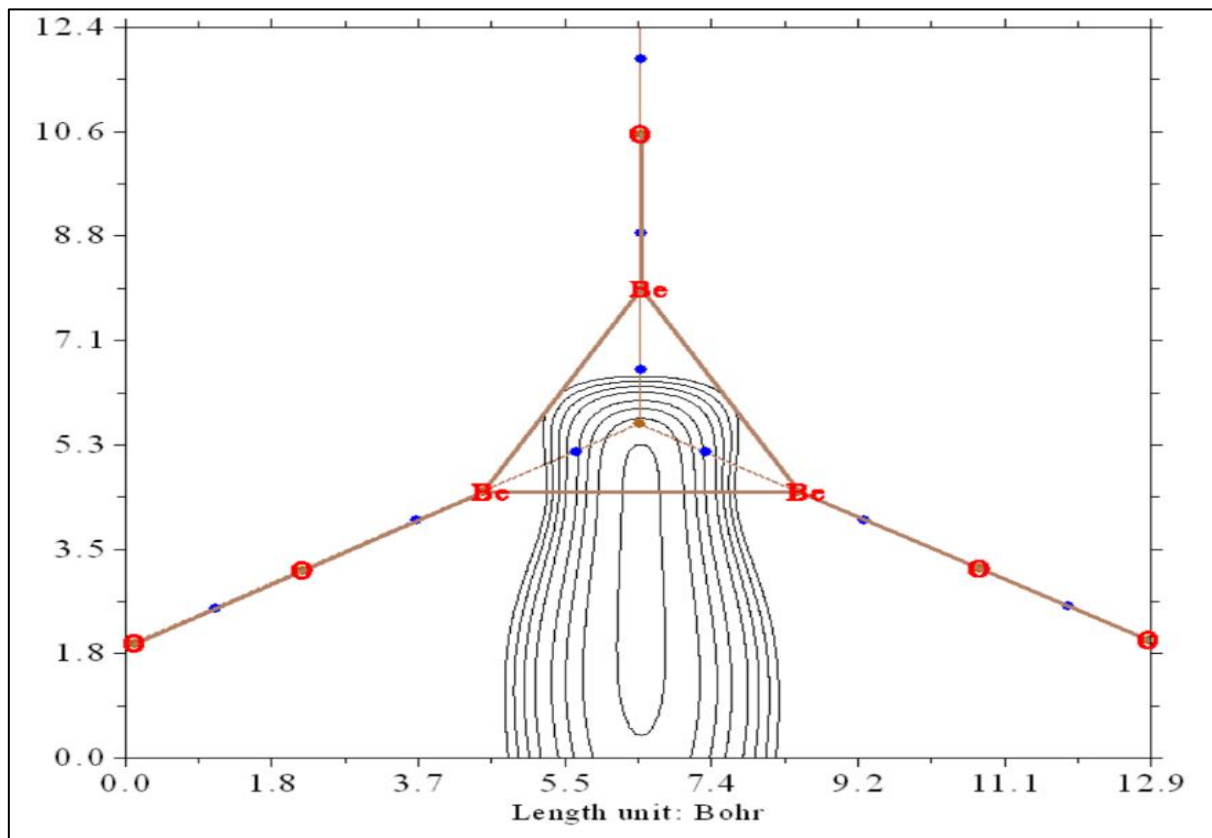


Fig 6 (b)

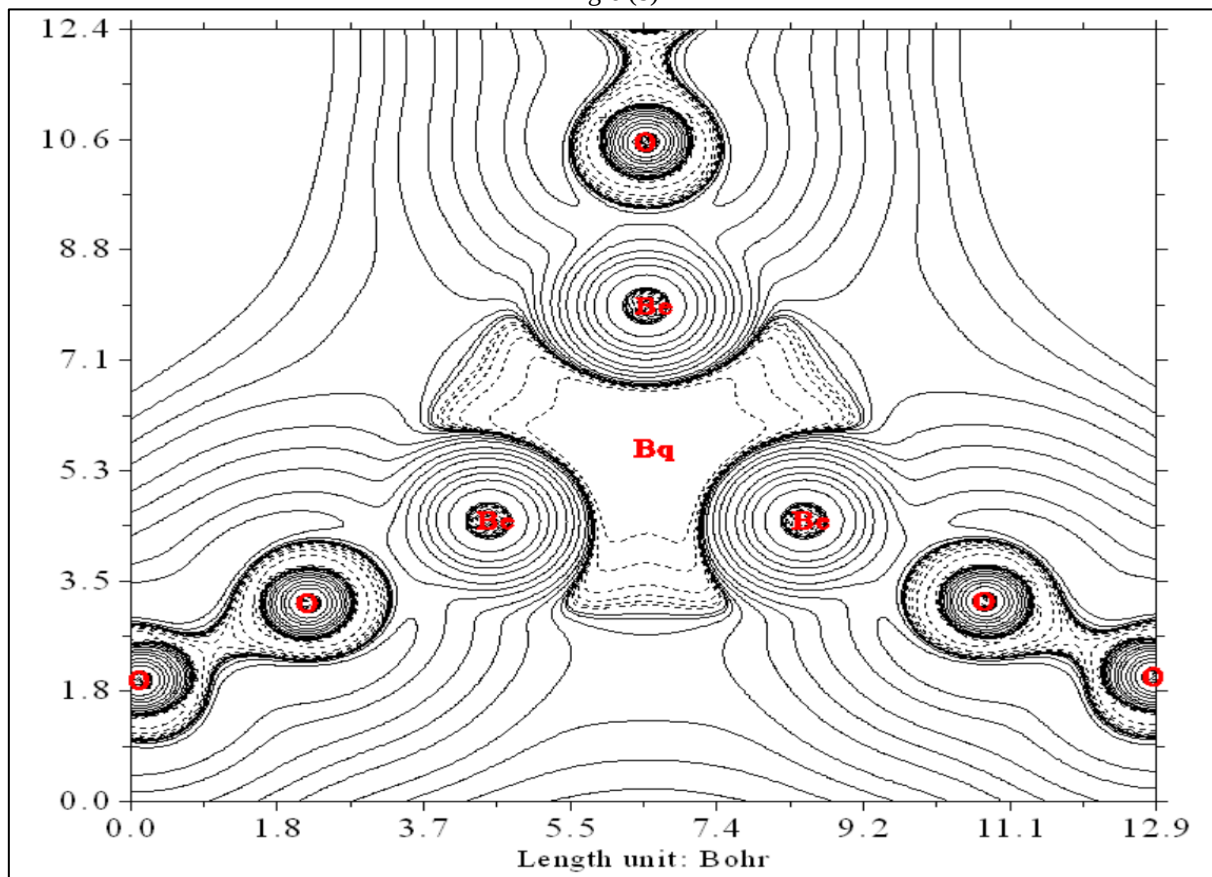


Fig 6 (c)

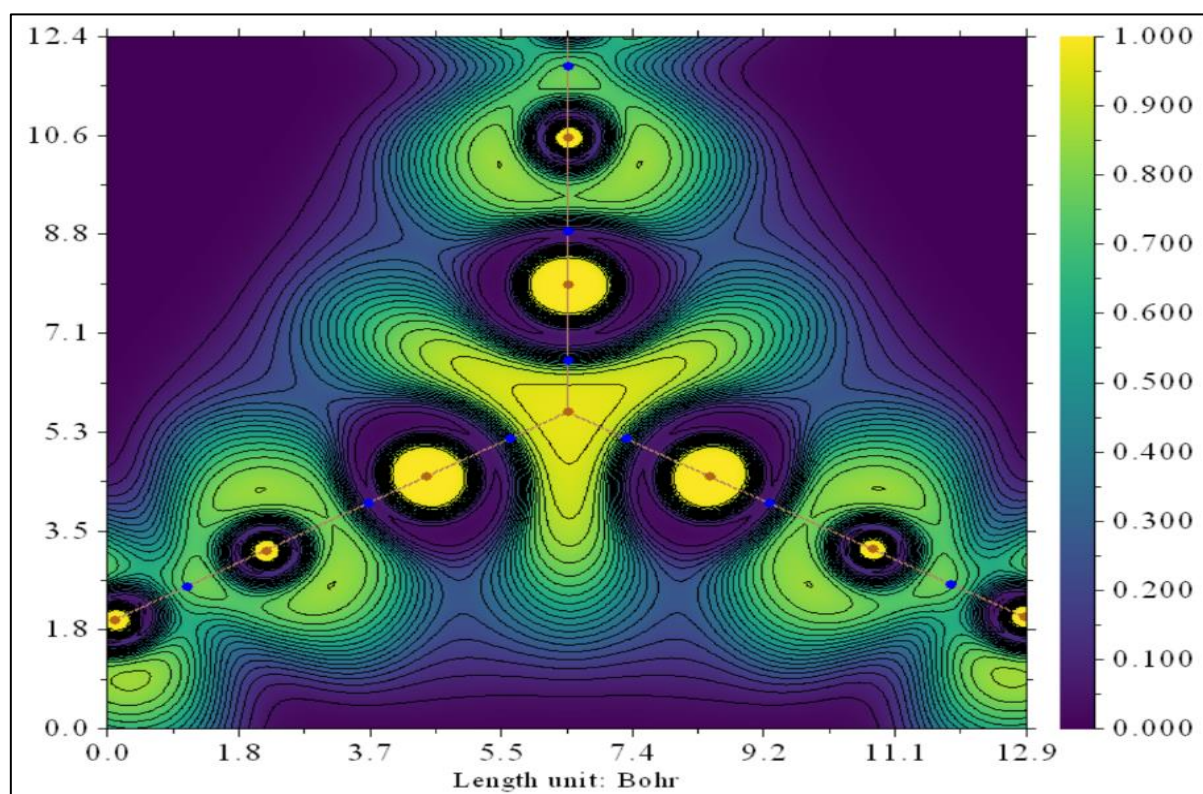


Fig 6 (d)

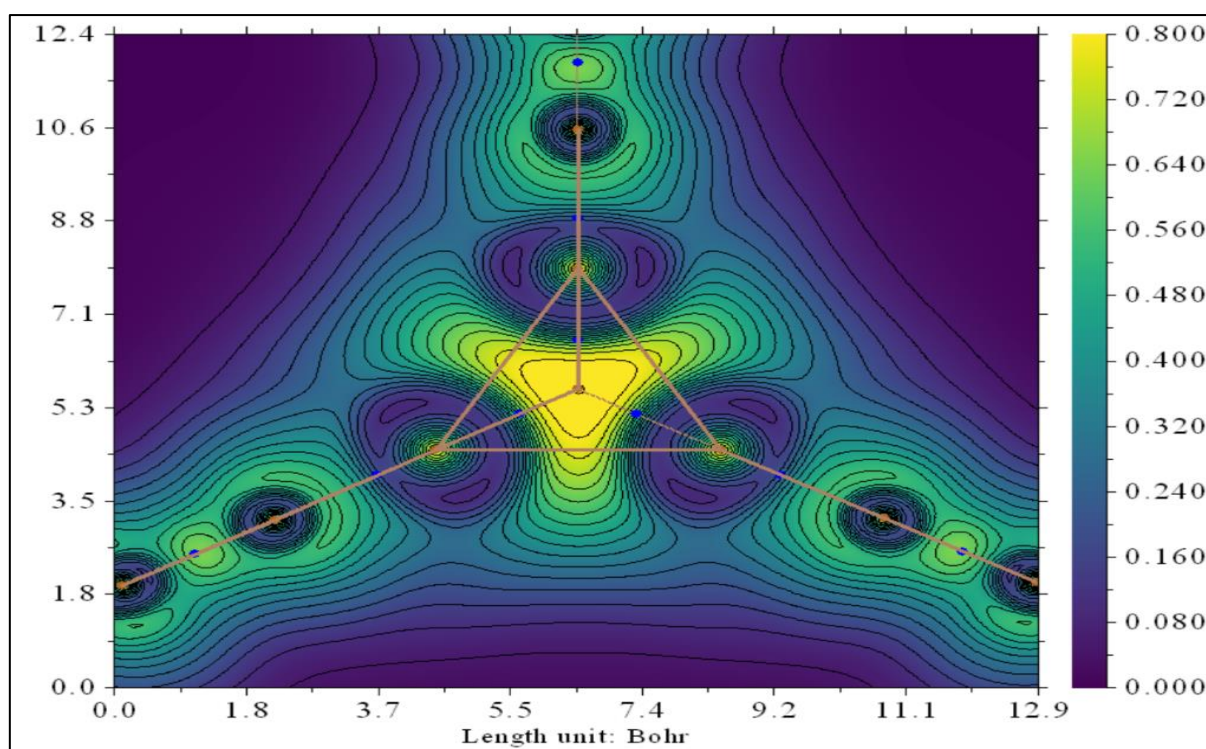


Fig 6 (e)

Fig 6 Two-dimensional contour and relief maps of the electron density and bonding descriptors across the Be_3 plane. (a) Total electron density (ρ) showing charge concentration at the ring centroid. (b) Becke overlap weight partitioning between Be_1 and Be_2 , indicating an open channel through the core. (c) Laplacian of electron density ($\nabla^2\rho$), highlighting the valence shell charge concentration ($\nabla^2\rho < 0$, dashed contours) around Bq . (d) Electron Localization Function (ELF) and (e) Localized Orbital Locator (LOL), identifying a trisynaptic basin at the Be_3 centroid (ELF ≈ 0.85 – 0.90 ; LOL > 0.75).

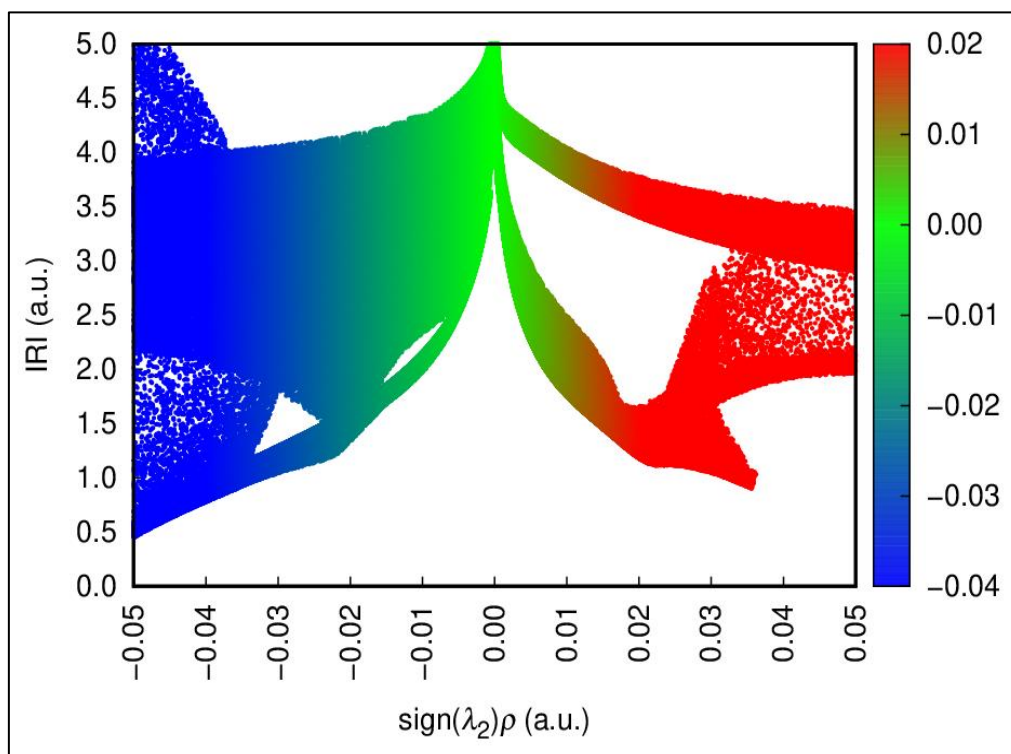


Fig 7 (a)

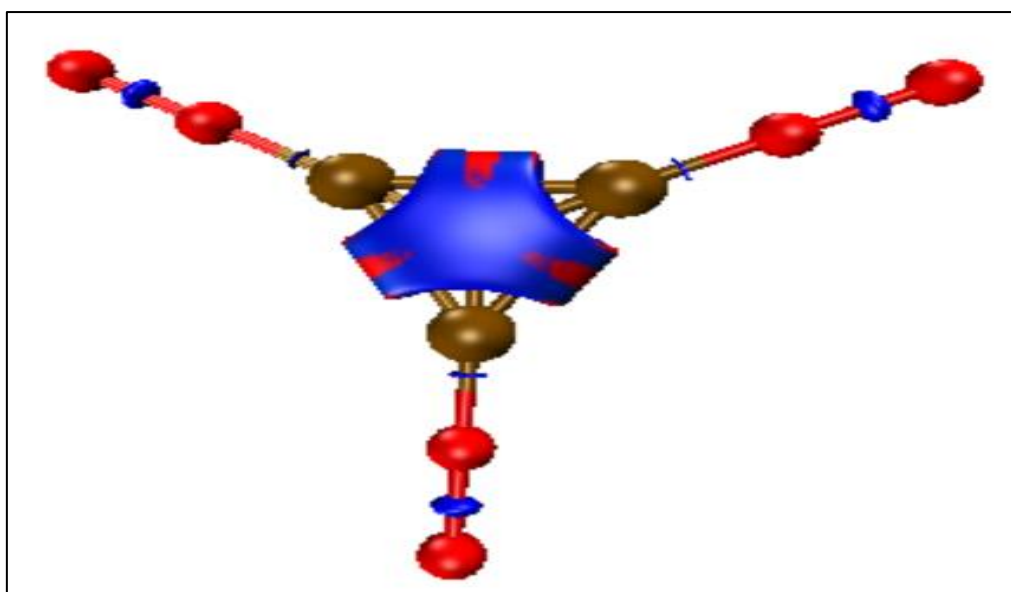


Fig 7 (b)

Fig 6 Non-covalent and covalent interaction analysis via the Interaction Region Indicator (IRI). (a) 2D scatter plot of IRI versus $\text{sign}(\lambda_2)\rho$, showing covalent features at $\text{sign}(\lambda_2)\rho < -0.035$ a.u. and delocalized attractive interactions between -0.015 and -0.030 a.u. (b) 3D IRI isosurface (isovalue = 1.0 a.u.), illustrating an attractive bonding domain (blue) filling the central Be_3 ring cavity and steric repulsion (red) along the inner periphery.

Direct (3,−1) saddle points between adjacent Be atoms are absent; instead, gradient paths from each Be nucleus terminate at the central NNA (Bq, CP 4) via BCPs 13, 14, and 15 (path lengths 2.290–2.306 Bohr). The NNA basin occupies 109.90 Bohr³ and provides the largest contribution (0.02378 a.u.) to the total density according to source function integration. In addition, both ELF and LOL show a pronounced attractor at the Be_3 centroid (ELF ≈ 0.85 –0.90; LOL > 0.75).

Delocalization index analysis corroborates this topology: direct pairwise Be–Be sharing is small (0.075–0.076), whereas delocalization between each Be center and the NNA is substantial (0.323–0.324). The sum across the three metal centers ($\sum \delta(\text{Be}_i, \text{Bq}) = 0.9707 \approx 1.0$ pair) quantitatively demonstrates that the Be_3 core forms an authentic three-center two-electron (3c–2e) σ -aromatic bond localized at the interstitial attractor. The IRI isosurfaces further illustrate that this shared electron domain encapsulates

the central cavity, shielding the three Be cores while driving electron transfer into the surrounding dioxygen ligands.

IV. CONCLUSIONS

The electronic structure of $\text{Be}_3(\text{O}_2)_3$ illustrates an unusual balance between multicenter metal–metal bonding, non-nuclear attractors, and small-molecule activation. DLPNO-CCSD(T) and ETS-NOCV calculations reveal that the complex is stabilized by large orbital interactions ($\Delta E_{\text{orb}} = -503.51$ kcal/mol) that drive electron transfer into the dioxygen π^* manifold. QTAIM analysis confirms that the Be_3 ring lacks classical pairwise Be–Be bond critical points, exhibiting instead an NNA-mediated star topology. Integrated source functions, electron localization indices (ELF/LOL), and delocalization matrices demonstrate that the cluster core is sustained by a central $3c-2e$ σ -aromatic bond, providing insight into low-valent alkaline-earth cluster chemistry.

➤ Associated Content

• Supporting Information

The Supporting Information is available free of charge at [ACS URL]. Cartesian coordinates of optimized geometries, additional computational details, and extended topological data (PDF).

➤ Notes

The authors declare no competing financial interest.

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