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Stabilization of Low-Valent Beryllium–Beryllium Units Through Charge-Shift Amido-Bridges and Core Aromaticity

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Abstract: We report the theoretical characterization of a unique amido-bridged beryllium cluster, $Be_4(N\text{-}Ar)_2$. Density functional theory (DFT) calculations at the TPSS/def2-TZVP level reveal a stable, planar six-membered Be_2-N-Be_2-N ring core. The structure features distinct covalent Be-Be single bonds (2.049 Å) within the dumbbells. Multi-method analyses including Natural Bond Orbital (NBO), Localized Orbital Locator (LOL), and Electron Localization Function (ELF) demonstrate that the core is stabilized by significant Nitrogen lone-pair donation into the electron-deficient Beryllium centers ($n_N \rightarrow Be$). Magnetic criteria (NICS(0) = -5.22 ppm) confirm the aromatic character of the framework. Furthermore, topological signatures from LOL and Laplacian mapping identify the Be-N bridges as possessing substantial charge-shift character.

Keywords: *NBO, LOL, Charge Shift Bond, ELF, Laplacian, Cotton Effect.*

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I. INTRODUCTION

The stabilization of Main Group metal-metal bonds remains a cornerstone of contemporary organometallic chemistry, with low-valent Beryllium derivatives posing significant synthetic and theoretical challenges.[1] While recent efforts have focused on carbene-stabilized diberyllocenes, the potential for amido ligands to bridge and stabilize Be-Be interactions is less understood.[2, 4] This study employs a suite of computational tools to delineate the bonding motifs, aromaticity, and spectroscopic properties of a model $Be_4(N\text{-}Ar)_2$ cluster.

II. COMPUTATIONAL METHODS

Geometry optimizations and vibrational frequency analyses were performed using ORCA 6.1.1 with the TPSS meta-GGA functional and the def2-TZVP basis set.[3, 10-12] Natural Bond Orbital (NBO) analysis was conducted to evaluate second-order perturbation energies.[5,6] Electronic localization and Laplacian topology were analyzed using Multiwfn.[7] Magnetic shielding (NICS) and excited-state (TD-DFT) properties were modelled at the same level of theory.

III. RESULTS AND DISCUSSION

➢ *Molecular Structure and Stability*

The optimized $Be_4(N\text{-}Ar)_2$ cluster maintains a planar core with Beryllium dumbbells. The interatomic Be-Be distance of 2.0488 Å and a Mayer bond order of 0.8525 signify a formal metal-metal single bond. The bridging Be-N distance of 1.5423 Å indicates strong coordination. Frequency analysis confirms the structure is a local minimum, with no imaginary modes and a calculated Gibbs free energy of -632.06038 Eh.

Table 1. Selected Structural and Electronic Parameters for $Be_4(N\text{-}Ar)_2$

Parameter	Value
Be-Be Distance	2.0488 Å
Be-N Distance	1.5423 Å
Mayer Bond Order (Be–Be)	0.8525
Mayer Bond Order (Be–N)	1.2946
NICS(0)	-5.22 ppm
NICS(1)	-1.19 ppm

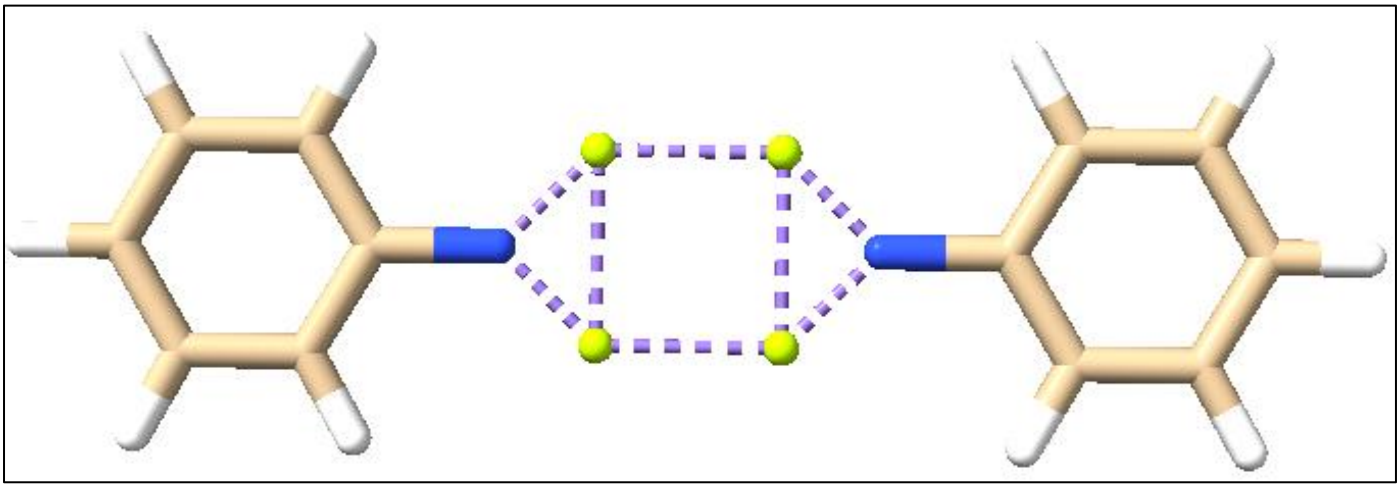

Fig 1 Optimized Molecular Structure of $Be_4(N\text{-}Ar)_2$

- *Electronic Bonding Analysis:*

NBO analysis reveals that the Be-Be interaction is a classic σ-bond. However, the stability of the six-membered ring core is primarily derived from $n_N \rightarrow$ Be dative interactions, where Nitrogen lone pairs donate into vacant Beryllium 2p orbitals. Natural atomic charges indicate that beryllium centres are positively polarised (+0.13), while amido nitrogens are negatively charged (+0.25 in Mulliken, but polarised in a dative context).

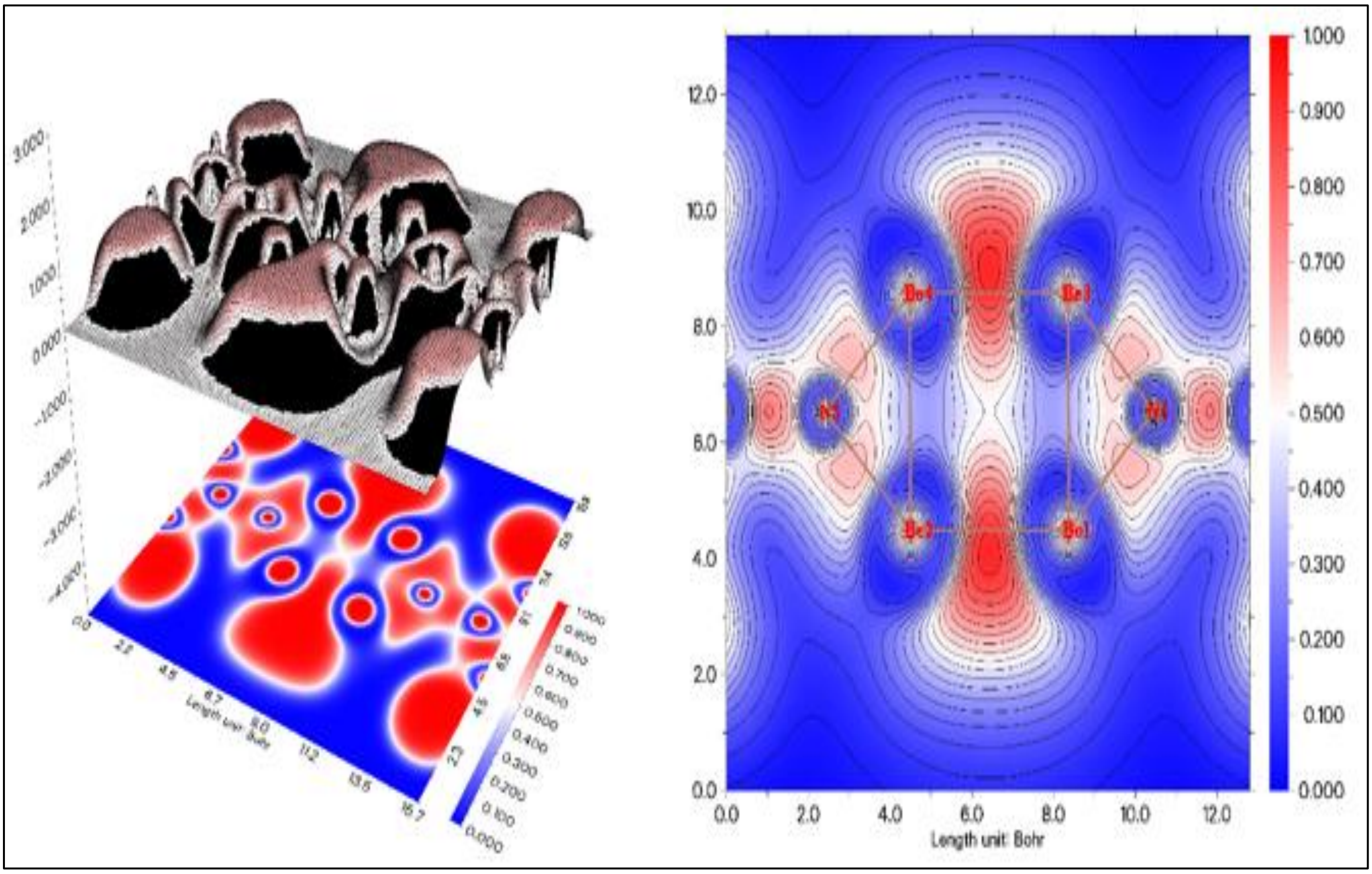

Fig 2 Localized Orbital Locator (LOL) and ELF Maps

- *Topological Properties:*

The ELF map shows clear disynaptic basins between Beryllium atoms, confirming covalent character. The LOL map and the Laplacian $(\nabla^2\rho)$ contour plot reveal "pinched" basins and charge depletion between Beryllium and Nitrogen. This is a definitive signature of Charge-Shift (CS) bonding, where resonance between ionic and covalent forms provides the majority of the bonding energy.[9,16-22]

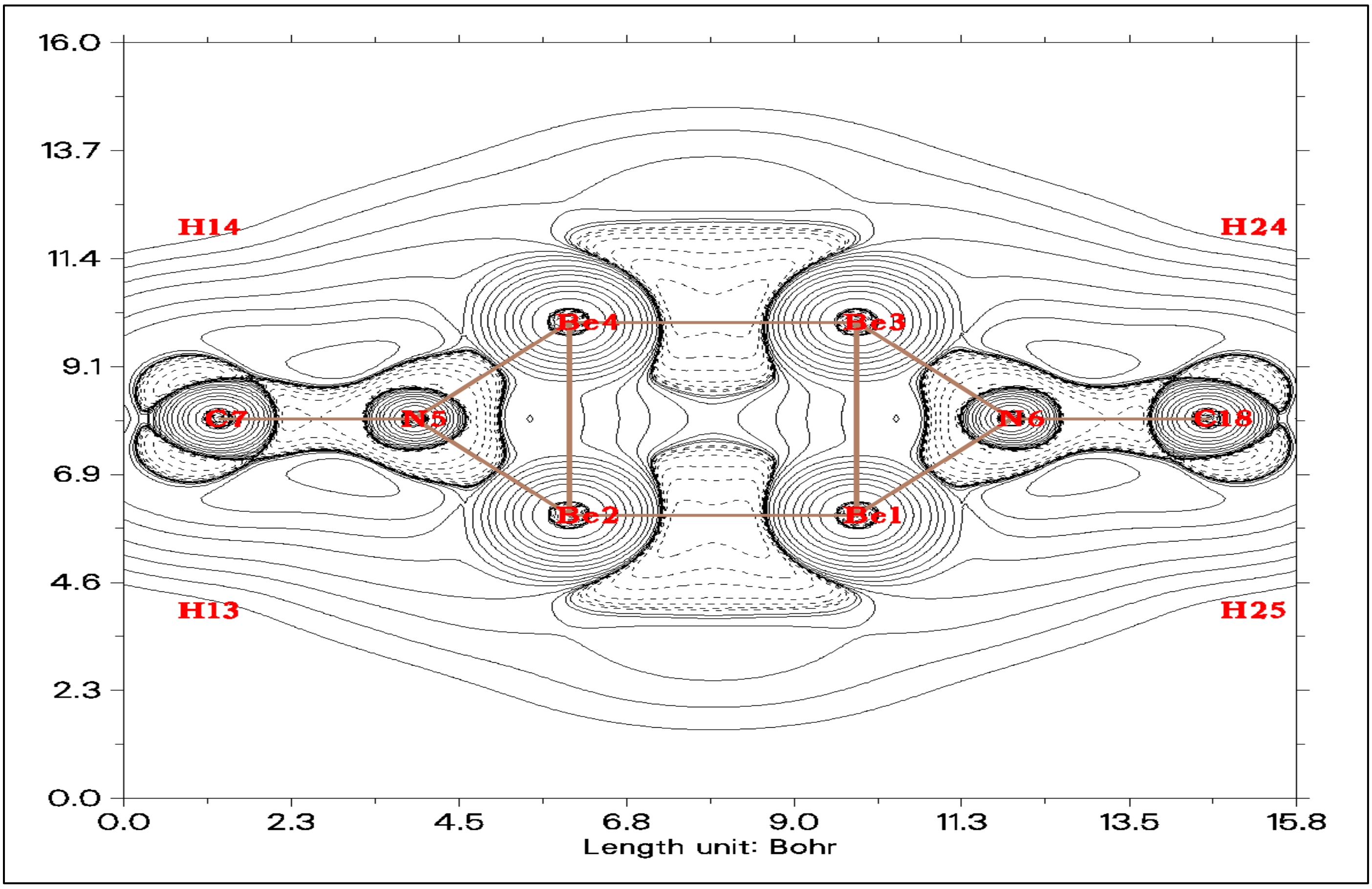

Fig 3 Contour Map of the Electron Density Laplacian ($\nabla^2\rho$)

- *Magnetic Aromaticity*

To test for delocalization, NICS values were calculated.[8] The NICS(0) value of -5.22 ppm indicates a moderate diatropic ring current at the geometric centre. The NICS(1) value of -1.19 ppm confirms that the core enjoys delocalized electronic character, classifying it as a weakly aromatic main-group cluster.

- *Electronic Spectroscopy* [13-15]

The TD-DFT simulated UV-Vis spectrum exhibits an intense absorption band at 360.5 nm (f = 0.782), assigned to the HOMO → LUMO+1 π-π* transition of the core. A secondary feature at 441.3 nm reflects $n_N \rightarrow Be_2\ \sigma^*$ charge transfer. The simulated ECD spectrum confirms the chiroptical activity of the cluster, featuring a sharp negative Cotton effect at 360 nm. The ECD profile further validates the delocalized nature of the core, as the intensity of the Cotton effects reflects the significant electronic communication across the Be_4N_2 framework.

Table 2 Summary of Key Excited States and Electronic Transitions

State	λ (nm)	F (Osc.)	Major Contributions
3	441.3	0.184	HOMO-2 → LUMO (77%)
6	360.5	0.782	HOMO → LUMO+1 (95%)

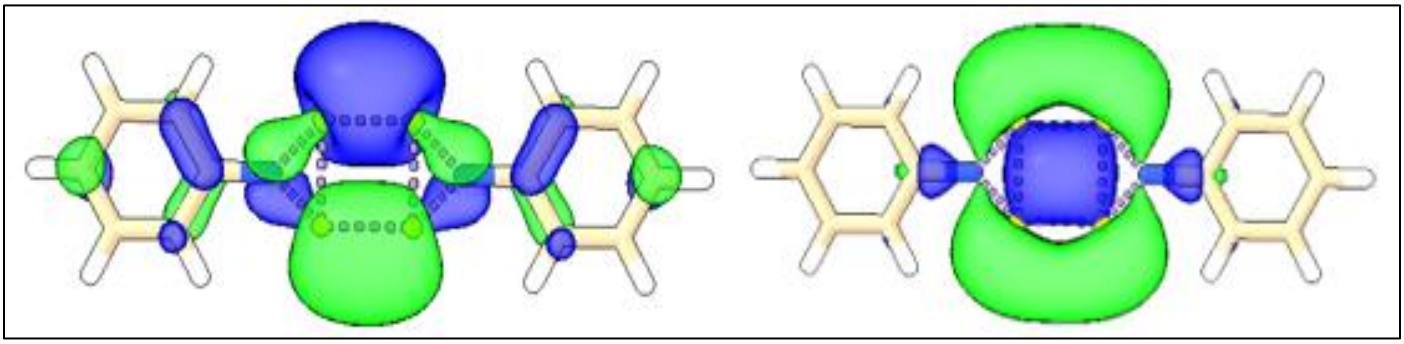

Fig 4 HOMO-2 and LUMO

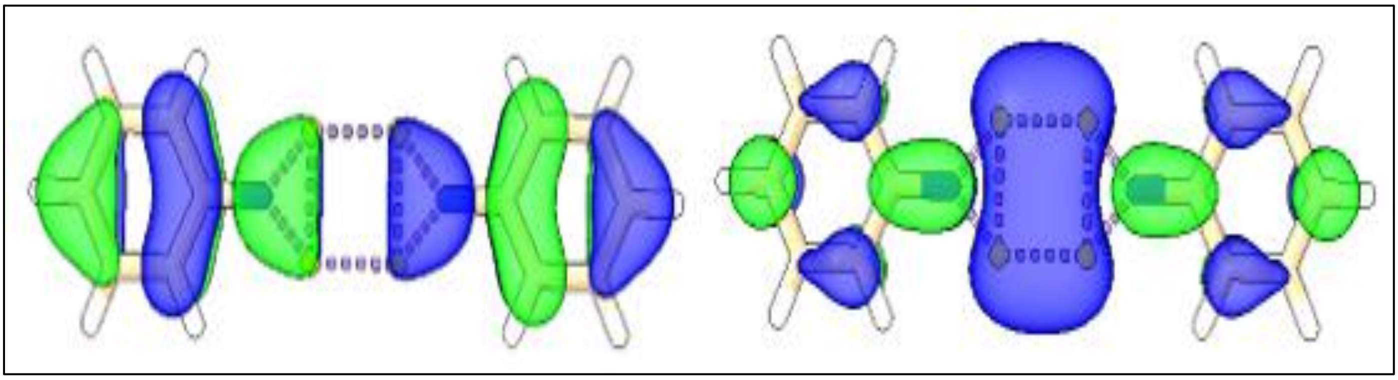

Fig 5 HOMO and LUMO+1

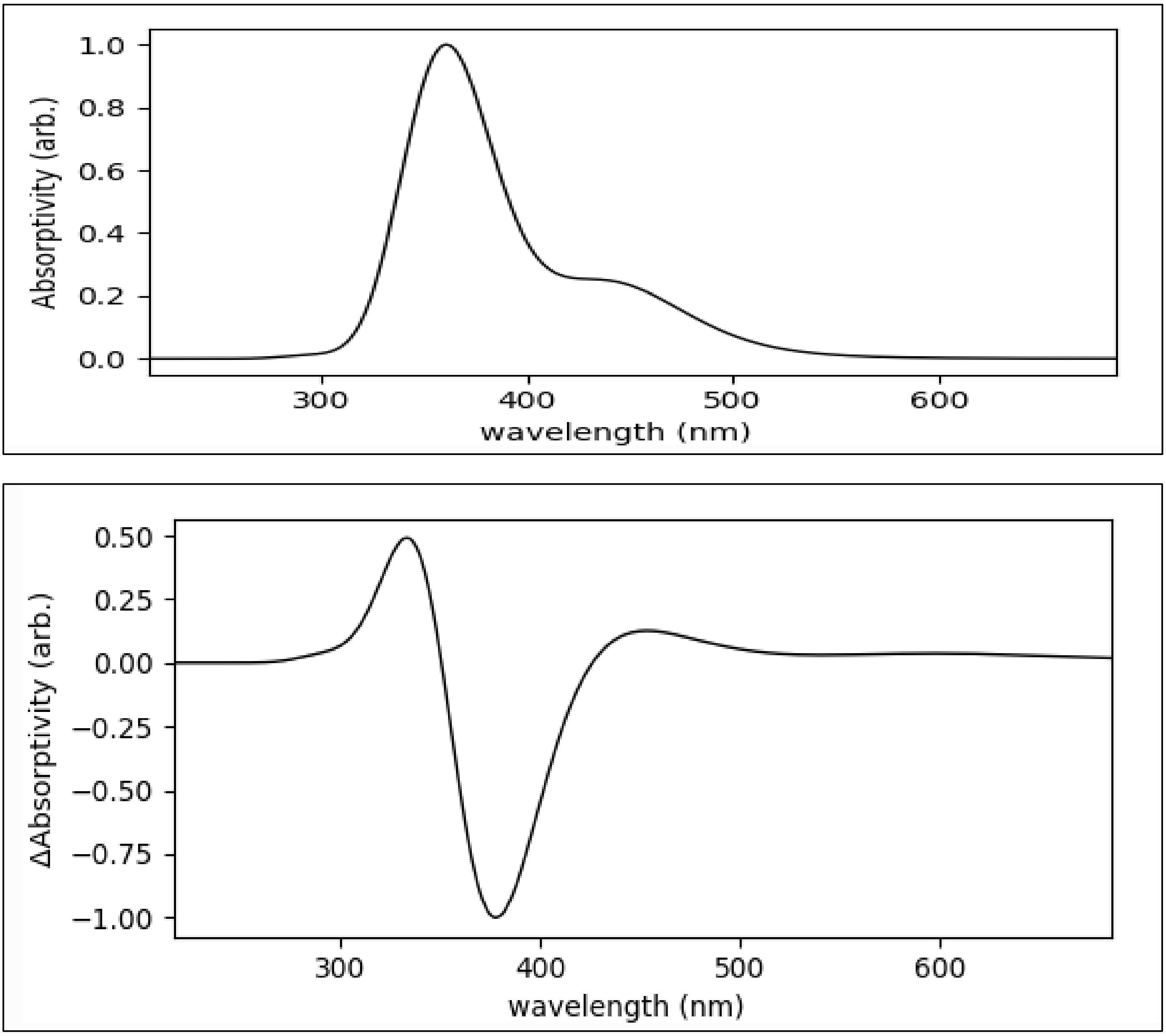

Fig 6 Simulated Absorption (UV-Vis) and ECD Spectra

IV. CONCLUSION

The $Be_4(N\text{-}Ar)_2$ cluster is a stable, aromatic main-group species characterized by a synergy of covalent Be-Be bonding and charge-shift Be-N bridging. These findings provide a theoretical foundation for the use of amido-bridges in the design of stable main-group metal clusters with delocalized electronic properties.

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