Supporting Information: Electronic Accommodation Versus Geometric Frustration in Doped Icosahedral Titanium Nanoclusters

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1 Introduction

Icosahedral transition-metal nanoclusters constitute a minimal and well-defined platform for probing the interplay between geometric frustration and electronic relaxation in finite systems. In this Supporting Information, pristine Ti$_{13}$ and doped Ti$_{12}$TM nanoclusters (TM = V, Fe, Ni, Pt) are employed as model systems to quantify the energetic and structural descriptors underlying the Principle of Competitive Stability (PCS) introduced in the main text.

The pristine Ti$_{13}$ nanocluster adopts an ideal icosahedral geometry, composed of one central atom and twelve symmetry-equivalent surface atoms. Doping is introduced by substitution either at the central (core) site or at one of the surface (shell) sites. These two substitutional motifs provide a controlled comparison between highly constrained and lower-coordination environments under identical topological conditions.

2 Density Functional Theory Calculations

Spin-polarized scalar-relativistic density functional theory (DFT) calculations were performed within the generalized gradient approximation using the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional[1–3]. The projector augmented-wave (PAW) method[4,5] as implemented in the Vienna *Ab-initio* Simulation Package (VASP)[6–8] was employed.

All nanoclusters were placed in a cubic supercell of side length 25 Å, ensuring a minimum vacuum separation of 14 Å. A plane-wave cutoff energy of 500 eV and Γ-point sampling were used. Structural relaxations were performed until residual forces were below 0.015 eV Å^{-1} and total energy convergence reached 1.0×10^{-6} eV.

3 Main Dataset

Table S1 summarizes all magnetic, geometric, energetic, and electronic descriptors used throughout the main text and Supporting Information. For clarity, each quantity is explicitly defined below.

- m_{tot}: total magnetic moment of the nanocluster.
- d_{av}: average bond lengths from effective coordination concept[9,10].
- ECN: effective coordination number (see Section 5).
- ΔE: site preference energy between central (c) and peripheral (p) substitution.
- ΔE_{dist}: distortion energy quantifying geometric frustration.
- ε_d: center of gravity of the occupied d-states relative to the Fermi level.
- E_b: binding energy per atom.
- ΔE_{int}: dopant–shell interaction energy.
- Δd_{av} deviation for d_{av} in relation to Ti_{13} case.
- ΔECN deviation for ECN in relation to Ti_{13} case.
- RMSD: root-mean-square deviation of the Ti shell relative to pristine Ti_{13}.
- $\langle d \rangle_{\mathrm{Ti–Ti}}$, $\langle d \rangle_{\mathrm{TM–Ti}}$: average nearest-neighbor bond length, defined using a cutoff of 3.3 Å.
- Δq_{c}, Δq_{p}, Δq_{TM}: Bader charges for central (c) and peripheral (p) regions and net dopant (TM) charge transfer.

In the next sections, we will explain the specific analyses performed.

Table S1: Summary of magnetic, structural, energetic, electronic, and geometric descriptors for doped $Ti_{12}TM$ nanoclusters with TM at central (c) and peripheral (p) sites.

System	m_{tot} (μ_B)	d_{av} (Å)	ECN	ΔE (eV)	ΔE_{dist} (eV)	ε_d (eV)	E_b (eV)	ΔE_{int} (eV)	Δd_{av} (%)	ΔECN (%)	RMSD (Å)	$\langle d \rangle_{\mathrm{Ti–Ti}}$ (Å)	$\langle d \rangle_{\mathrm{TM–Ti}}$ (Å)	Δq_{c} (e)	Δq_{p} (e)	Δq_{TM} (e)
$Ti_{12}V$ (c)	5	2.6761	6.3633	-0.72807	0.14998	-0.74744	-3.74657	-0.72802	-1.131	-0.519	0.302	3.165	2.923	-0.44330	+0.44330	-0.44330
$Ti_{12}V$ (p)	5	2.6837	6.2922		0.52872	-0.71591	-3.69057	-0.48509	-0.850	-1.631	0.495	3.169	2.886	-0.64681	+0.64681	-0.77034
$Ti_{12}Fe$ (c)	2	2.6384	6.3937	-0.62182	0.00580	-0.92114	-3.76255	-0.72958	-2.523	-0.044	0.204	3.157	2.871	-1.98316	+1.98316	-1.98316
$Ti_{12}Fe$ (p)	2	2.6552	6.1997		0.44251	-0.88402	-3.71472	-0.50063	-1.903	-3.077	0.503	3.171	2.882	-0.35818	+0.35818	-1.24142
$Ti_{12}Ni$ (c)	0	2.6493	6.3965	-0.07386	0.02234	-1.10692	-3.73194	-0.70062	-2.121	0.000	0.218	3.159	2.876	-1.55779	+1.55779	-1.55779
$Ti_{12}Ni$ (p)	0	2.6705	6.2852		0.11517	-1.09078	-3.72626	-0.47943	-1.337	-1.740	0.512	3.173	2.879	-0.38490	+0.38490	-1.20670
$Ti_{12}Pt$ (c)	0	2.7000	6.3965		0.21122	-1.66780	-3.85378	-0.84135	-0.248	0.000	0.286	3.163	2.915	-2.96356	+2.96356	-2.96356
$Ti_{12}Pt$ (p)	0	2.6849	6.2910	+0.56171	0.20816	-1.47620	-3.89699	-0.65946	-0.805	-1.649	0.509	3.170	2.905	-0.30401	+0.30401	-1.61493

4 Energy Analysis

The binding energy (E_b) is defined as:

$$E_b = E_{\text{cluster}} - \sum_{i=1}^{N} E^i_{\text{atom}} \ , \tag{1}$$

where E^i_{atom} is the energy of isolated atom i.

The site preference energy (ΔE) quantifies the relative stability of central (c) *versus* peripheral (p) doping:

$$\Delta E = E_{\text{TM-c}} - E_{\text{TM-p}} \ , \tag{2}$$

where $E_{\text{TM-c}}$ and $E_{\text{TM-p}}$ are total energies of nanoclusters with TM in central and peripheral positions, respectively. Negative values indicate central site preference.

The distortion energy (ΔE_{dist}) isolates the energetic cost associated with enforcing the nanocluster topology:

$$\Delta E_{\text{dist}} = E_{\text{relaxed shell}} - E_{\text{frozen shell}} \ , \tag{3}$$

where the distortion energy is the energy difference between the frozen $E_{\text{frozen shell}}$, without TM atom, and the optimized $E_{\text{relaxed shell}}$ systems.

The dopant–shell interaction energy is defined as

$$\Delta E_{\text{int}} = E_{\text{TM-shell}} - \left(E_{\text{TM}} + E_{\text{shell}}\right) \ , \tag{4}$$

where E_{TM} is the energy of isolated TM atom, and E_{shell} is the energy of the Ti shell with the dopant removed.

5 Effective Coordination Number

The effective coordination number (ECN) is evaluated following Hoppe's definition[9,10]:

$$\text{ECN}_i = \sum_j \exp\left[1 - \left(\frac{d_{ij}}{d_0}\right)^6\right] \ , \tag{5}$$

where d_{ij} is the interatomic distance and d_0 is a normalization distance determined self-consistently.

Unlike the conventional coordination number (CN), which counts neighbors within a sharp cutoff, ECN provides a continuous, distance-weighted measure of local coordination, making it particularly suitable for distorted finite systems.

Average bond lengths are defined as

$$d_{\text{av}} = \frac{1}{N_{\text{pairs}}} \sum_{i<j} d_{ij} \ . \tag{6}$$

Both, ECN and d_{av} were evaluated to assess the applicability of conventional geometric descriptors to site preference. Although central substitution systematically yields higher ECN values than peripheral substitution, no direct correlation is observed between ECN and site preference energy $\Delta E_{\text{in-out}}$. Similarly, variations in d_{av} are modest across different dopants and do not track the observed stability trends.

Relative deviations are computed with respect to pristine Ti$_{13}$:

$$\Delta d_{\text{av}} = \frac{d_{\text{av}} - d_{\text{av}}^{\text{Ti}_{13}}}{d_{\text{av}}^{\text{Ti}_{13}}} \times 100\% \ , \quad \Delta \text{ECN} = \frac{\text{ECN} - \text{ECN}^{\text{Ti}_{13}}}{\text{ECN}^{\text{Ti}_{13}}} \times 100\% \ . \tag{7}$$

6 Electronic Structure Analysis

The center of gravity of the occupied d-states ε_d relative to the Fermi level was calculated as the first moment of the projected d-density of states (PDOS):

$$\varepsilon_d = \frac{\int_{-\infty}^{E_F} E \rho_d(E) \, dE}{\int_{-\infty}^{E_F} \rho_d(E) \, dE} \ , \tag{8}$$

where $\rho_d(E)$ is the d-PDOS and E_F is the Fermi energy. The d-band center serves as a compact descriptor of electronic flexibility and hybridization strength within the Hammer–Nørskov model[11,12]. Based on ε_d, in relation to the Fermi level, we can highlight the transition metal dopants with shallower d bands (states close to E_F) and with very deep d bands (rigid states), which exhibit, respectively, ease of re-hybridization and low capacity to accommodate stress.

Atomic charges were obtained using the Bader partitioning scheme[13,14], where the electronic density is divided into zero-flux regions:

$$\nabla\rho(\mathbf{r})\cdot\mathbf{n}(\mathbf{r}) = 0\,. \tag{9}$$

The charge transfer Δq is defined as:

$$\Delta q = q_{\text{atom}} - Z_{\text{valence}}\,, \tag{10}$$

where q_{atom} is the Bader charge and Z_{valence} is the number of valence electrons.

7 RMSD Analysis

Structural distortion was quantified using the root-mean-square deviation (RMSD) of the Ti shell relative to pristine Ti_{13}, excluding the dopant atom. RMSD was computed using optimal Kabsch alignment[15]. The central/peripheral dopant atom was excluded from the RMSD calculation to isolate the geometric response of the Ti framework. The RMSD was computed as

$$\text{RMSD} = \sqrt{\frac{1}{N}\sum_{i=1}^{N}\left|\mathbf{r}_i^{\text{doped}} - \mathbf{r}_i^{\text{ref}}\right|^2}\,, \tag{11}$$

where $\mathbf{r}_i^{\text{doped}}$ and $\mathbf{r}_i^{\text{ref}}$ are the atomic positions of the i-th Ti atom in the doped and pristine Ti_{13} nanoclusters, respectively, after optimal rigid-body alignment using the Kabsch algorithm[15].

Central substitution yields uniformly low RMSD values (0.20 Å to 0.30 Å), indicating isotropic shell relaxation. The dopant acts as a new core, to which the 12 Ti atoms adjust uniformly. Peripheral substitution produces significantly larger RMSD values ($\approx$ 0.51 Å), largely independent of dopant identity. This indicates that structural distortion is governed primarily by site topology, with only a weak dependence on chemical identity. The shell responds cooperatively and asymmetrically, redistributing the strain across multiple Ti-Ti bonds.

Qualitatively, the factor of $\sim$2 difference in RMSD between peripheral and central doping highlights a relation given by:

$$\Delta_{\text{geo}} \sim \mathscr{S}_{\text{site}} \,, \tag{12}$$

where Δ_{geo} is the geometric distortion and $\mathscr{S}_{\text{site}}$ is a generalized site stiffness factor. The peripheral site, involved in multiple bonds defining the shell's integrity, has a much higher $\mathscr{S}_{\text{site}}$ than the central site, which is coordinatively saturated but less critical for maintaining the shell's topology. The consistent RMSD for peripheral dopants suggests a common relaxation pathway, likely converging to a local energy minimum where the strain from the mismatched vertex is partially delocalized. In contrast, central doping preserves the point-group symmetry, leading to a simpler, one-parameter relaxation (uniform shell expansion/contraction).

8 Average Bond-Length Trends

The average bond length analysis $\langle d \rangle$ reveals local chemical bonding adjustments. Consequently, we investigate how both dopant position (central *versus* peripheral) and identity affect Ti-Ti and TM-Ti bond lengths, uncovering the physical hierarchy governing geometric response in doped icosahedral nanoclusters. The $\langle d \rangle$ values were calculated as:

$$\langle d \rangle_{X-Y} = \frac{1}{N_{\text{pairs}}} \sum_{i<j} d_{ij} \quad \text{for} \quad d_{ij} < 3.3\,\text{Å} \,, \tag{13}$$

where d_{ij} is the distance between atoms i and j, and the cutoff 3.3 Å captures first-neighbor interactions in icosahedral geometry.

Two bond categories were analyzed, (*i*) $\langle d \rangle_{\text{Ti–Ti}}$: average distance among the 12 Ti atoms in the shell (66 pairs for pristine, 55 pairs for peripheral doping where one Ti is replaced by TM); (*ii*) $\langle d \rangle_{\text{TM–Ti}}$: average distance between dopant (TM) and surrounding Ti atoms (12 for central, 5 for peripheral doping).

The Ti-Ti shell bonds exhibit consistent expansion upon doping, for central doping: $\Delta\langle d \rangle =$ 0.009 Å to 0.017 Å and for peripheral doping: $\Delta\langle d \rangle = 0.021$ Å to 0.025 Å. Peripheral doping induces approximately twice the shell expansion of central doping. The variation among different peripheral dopants is minimal (±0.002 Å), suggesting a dopant-independent response.

On the other hand, for central dopants, TM-Ti bond lengths follow a clear steric sequence:

$$\mathrm{Fe}\ (2.871\,\text{Å}) < \mathrm{Ni}\ (2.876\,\text{Å}) < \mathrm{Pt}\ (2.915\,\text{Å}) < \mathrm{V}\ (2.923\,\text{Å})\,. \tag{14}$$

This order correlates with metallic radii (Fe: 1.26 Å, Ni: 1.24 Å, Pt: 1.39 Å, V: 1.34 Å) rather than electronic properties like electronegativity or d-electron count.

For central dopants, the TM-Ti bond length ordering follows metallic radii, not electronic properties. If electronic effects dominated, we would expect grouping by periodic table column or electronegativity. Instead, Fe and Ni (similar radii) cluster together despite different d-electron configurations, while Pt ($5d$) and V ($3d$) group separately based on size. The minimal variation in $\Delta\langle d\rangle_{\mathrm{Ti-Ti}}$ among different peripheral dopants further supports steric dominance: the icosahedral shell responds similarly to any vertex substitution, regardless of chemical identity. When TM occupies the center, the Ti shell expands isotropically (small $\Delta\langle d\rangle_{\mathrm{Ti-Ti}}$), TM-Ti bonds adjust to accommodate size mismatch, and the icosahedral symmetry is preserved. This buffering effect minimizes strain propagation through the nanocluster. In contrast, peripheral doping creates localized strain that propagates through the shell, causing larger Ti-Ti expansion. The near-constant $\Delta\langle d\rangle_{\mathrm{Ti-Ti}}$ for peripheral doping (0.021 Å to 0.025 Å) reveals the icosahedral shell's collective mechanical response. The shell behaves as a cooperative network where local perturbation induces predictable global distortion. This spring constant of the icosahedral topology attenuates chemical differences among dopants.

Central doping induces modest, nearly isotropic expansion of the Ti shell, while TM–Ti bond lengths adjust according to dopant size. Peripheral substitution leads to larger shell expansion, reflecting cooperative strain propagation within the icosahedral network. The weak dopant dependence of peripheral distortions highlights the dominance of geometric frustration over chemical identity in this regime. These trends are consistent with the relaxation mechanisms discussed in the main text.

9 Electronic Accommodation and Site Preference Classification

For completeness, we summarize here how the energetic and electronic descriptors jointly rationalize site preference across the studied dopants.

The electronic signatures discussed in the main text are directly correlated with the distortion energy findings rather than with coordination number alone, which highlights the breakdown of purely geometric stability descriptors at the sub-nanometer scale. This observation underscores the necessity to treat electronic accommodation as an independent variable governing stability in finite systems. Within the PCS framework, symmetry breaking, inverted site preferences, and non-monotonic stability trends arise as direct energetic consequences of the competition between frustration-induced distortion and electronically driven relaxation.

Accordingly, V, Fe, and Ni satisfy the condition $\Delta E < 0$, stabilizing substitution at the central site. These dopants interact strongly with the Ti shell ($\Delta E_{\text{int}} < 0$), minimize ΔE_{dist}, and possess electronically flexible *d* states that enable compensatory charge redistribution under geometric frustration. In contrast, Pt satisfies $\Delta E > 0$ and preferentially occupies the peripheral site. Although Pt also exhibits strong interaction with the Ti network, it imposes a substantially larger distortion cost at the core, reflecting its deep and electronically rigid *d* band, which hinders frustration accommodation. As a result, strong bonding and large charge transfer alone are insufficient to stabilize highly coordinated environments in finite systems, leading to an inverted site preference.

References

1 Hohenberg, P.; Kohn, W. Inhomogeneous Electron Gas. *Phys. Rev.* **1964**, *136*, B864–B871, DOI: `10.1103/PhysRev.136.B864`.

2 Kohn, W.; Sham, L. J. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev.* **1965**, *140*, A1133–A1138, DOI: `10.1103/PhysRev.140.A1133`.

3 Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868, DOI: `10.1103/PhysRevLett.77.3865`.

4 Blöchl, P. E. Projector Augmented-Wave Method. *Phys. Rev. B* **1994**, *50*, 17953–17979, DOI: `10.1103/PhysRevB.50.17953`.

5 Kresse, G.; Joubert, D. From Ultrasoft Pseudopotentials to the Projector Agumented-Wave Method. *Phys. Rev. B* **1999**, *59*, 1758–1775, DOI: `10.1103/PhysRevB.59.1758`.

6 Kresse, G.; Hafner, J. Ab Initio Molecular Dynamics for Open-Shell Transition Metals. *Phys. Rev. B* **1993**, *48*, 13115–13126, DOI: `10.1103/PhysRevB.48.13115`.

7 Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys. Rev. B* **1996**, *54*, 11169–11186, DOI: `10.1103/PhysRevB.54.11169`.

8 Hafner, J. $Ab-initio$ simulations of materials using VASP: Density-functional theory and beyond. *J. Comput. Chem.* **2008**, *29*, 2044–2078, DOI: `10.1002/jcc.21057`.

9 Hoppe, R. The Coordination Number – an "Inorganic Chameleon". *Angew. Chem. Int. Ed.* **1970**, *9*, 25–34, DOI: `10.1002/anie.197000251`.

10 Hoppe, R. Effective Coordination Numbers (ECoN) and Mean Active Fictive Ionic Radii (MEFIR). *Z. Kristallogr.* **1979**, *150*, 23–52, DOI: `10.1524/zkri.1979.150.1-4.23`.

11 Hammer, B.; Nørskov, J. K. Electronic Factors Determining the Reactivity of Metal Surfaces. *Surf. Sci.* **1995**, *343*, 211–220, DOI: `10.1016/0039-6028(96)80007-0`.

12 Hammer, B.; Nørskov, J. K. *Advances in Catalysis*; Academic Press Inc, San Diego, 2000.

13 Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; International Series of Monographs on Chemistry; Clarendon Press, 1994.

14 Tang, W.; Sanville, E.; ; Henkelman, G. A Grid-Based Bader Analysis Algorithm without Lattice Bias. *J. Phys. Condens. Matter.* **2009**, *21*, 084204, DOI: `10.1088/0953-8984/21/8/084204`.

15 Kabsch, W. A solution for the best rotation to relate two sets of vectors. *Acta Crystallographica Section A: Crystal Physics, Diffraction, Theoretical and General Crystallography* **1976**, *32*, 922–923, DOI: `10.1107/S0567739476001873`.