Scan to Paper

Snap-shots of Cluster Growth: Electronic Structures of a Zintl Ion with a Linear Fe_3 Core, $[Fe_3Sn_{18}]^{4-}$

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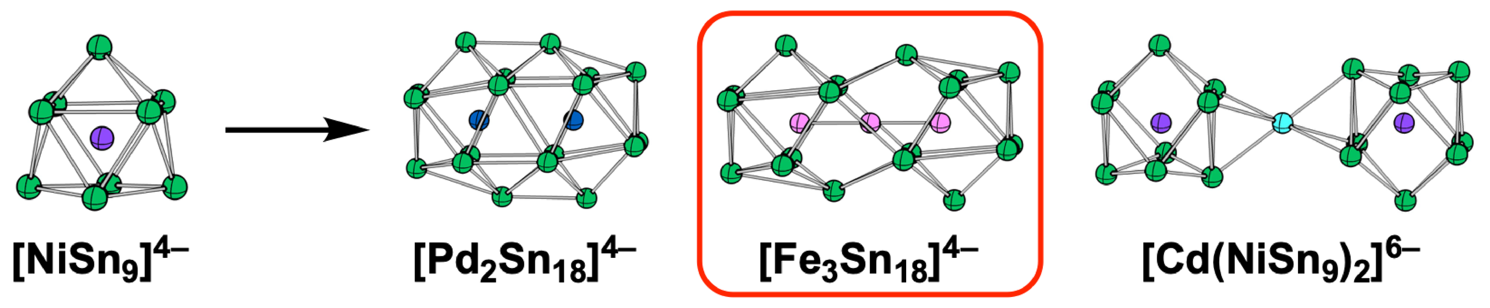
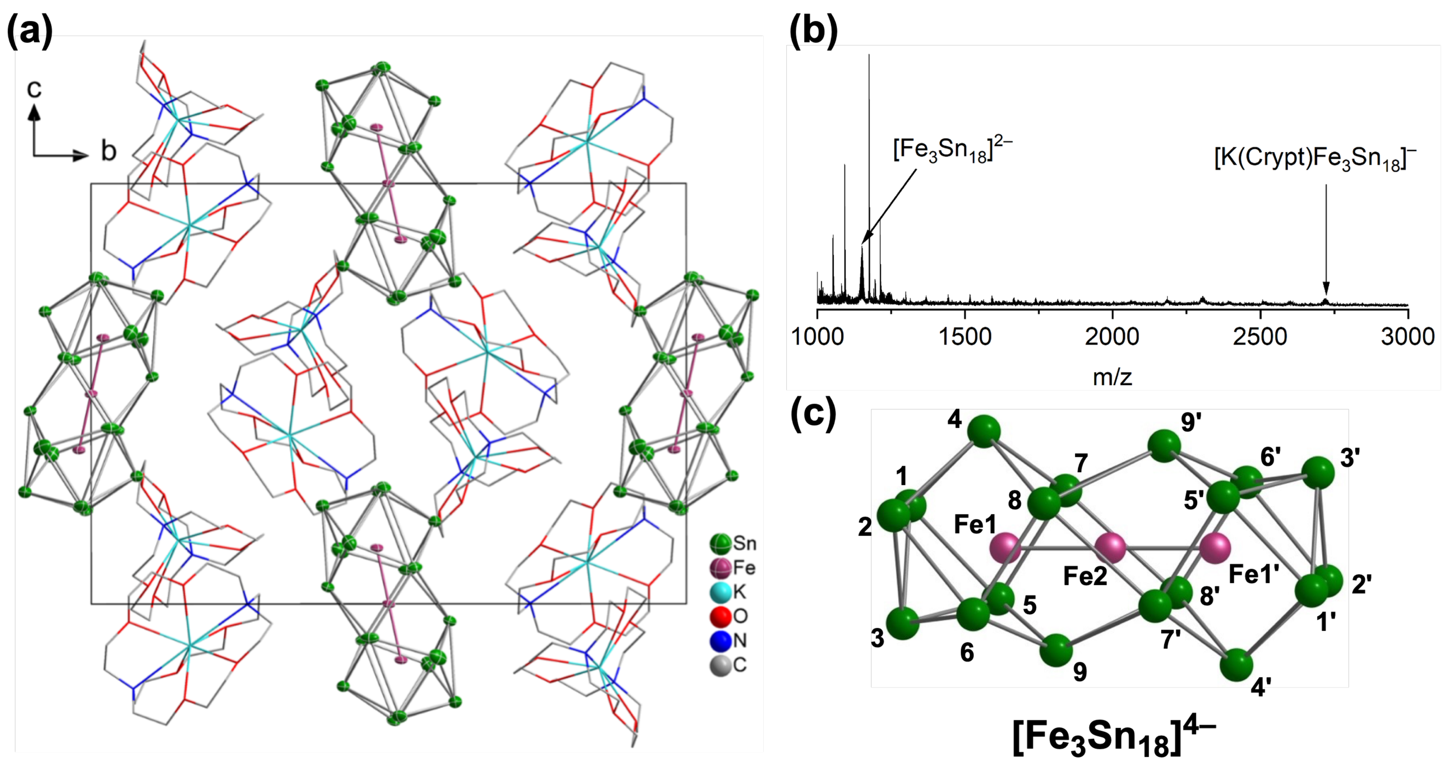
Introduction

- The research on Endohedral Zintl clusters extends from mono-cage to fused-cage clusters, where those with **18-vertex** cages composed of group 14 elements have been extensively investigated.
- Here, we report a new Sn_{18}-based cluster - **$[Fe_3Sn_{18}]^{4-}$**, with a linear Fe_3 core inside.[1] Its geometry is similar to existing D_{3d}-$[M_xSn_{18}]^{n-}$ examples,[2,3] but in an **intermediate bonding state** between two Sn_9 fragments.



Experimental and Computational Methods

- K_4Sn_9 + 2.2.2-crypt + $[K(thf)Fe(Ot\text{-}Bu)_3]_2$ $\rightarrow$ $[K(2.2.2\text{-crypt})]_4[Fe_3Sn_{18}]$ (10% yield based on the K_4Sn_9 precursor)



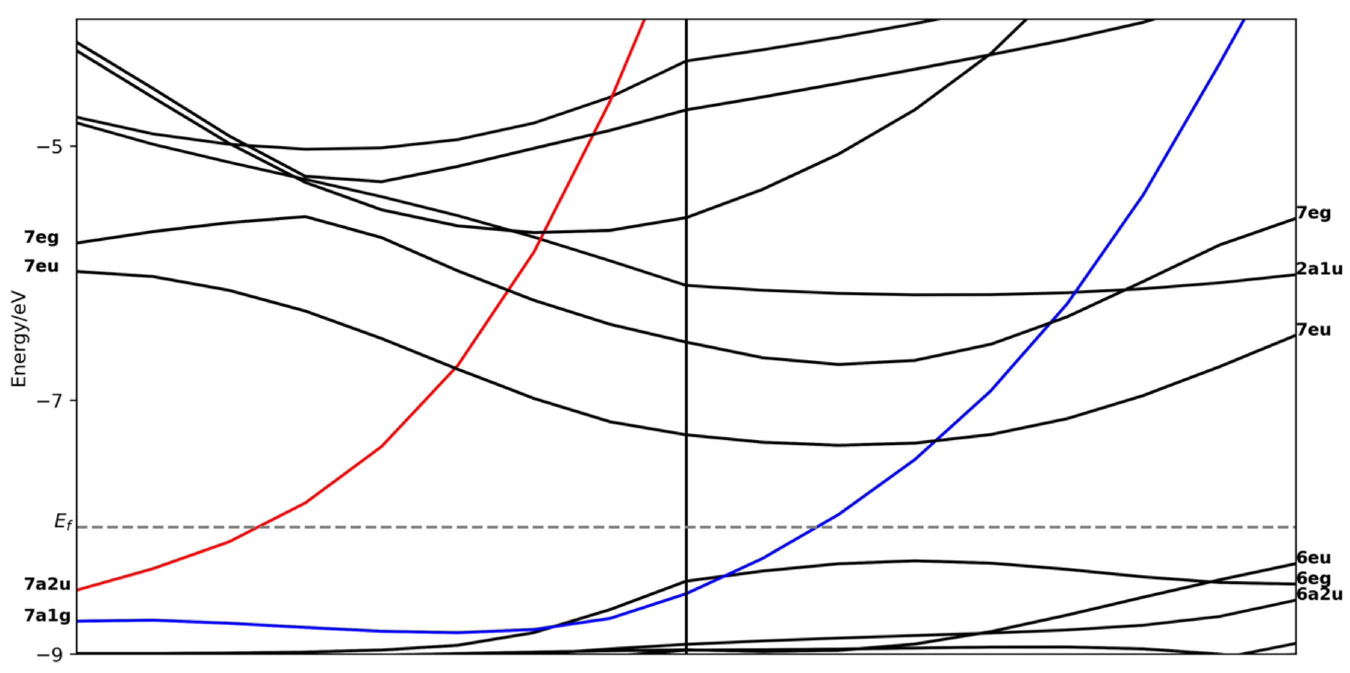
- All calculations were performed using the ADF 2021.104 package at **PBE/TZ2P** level, where the relativistic effect was considered by **ZORA**. The Walsh diagram was plotted individually with Python.

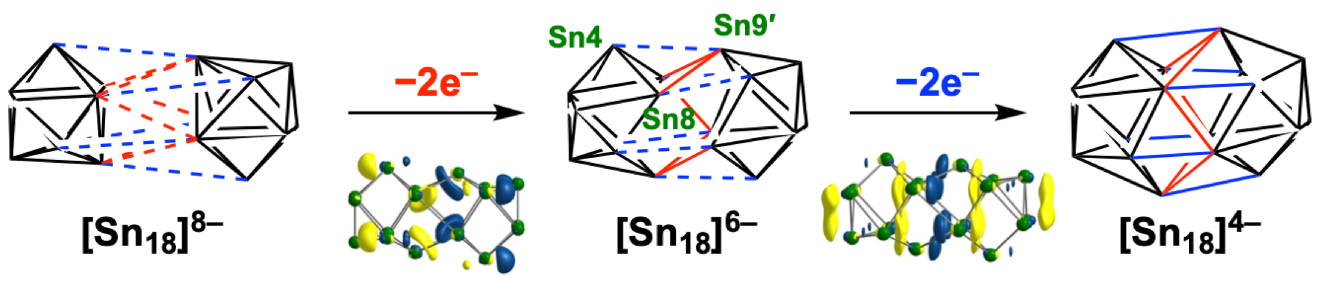
Cluster Growth Mechanism

- The cage structure of $[Fe_3Sn_{18}]^{4-}$ is as a middle-state between the **separated-limit** $[Cd(NiSn_9)_2]^{6-}$ and the **fused-limit** $[Pd_2Sn_{18}]^{4-}$ cases, as is the charge.

		E2-E8	E2-E4	E6-E9	E8-E9′	E4-E9′
$[Sn_{18}]^{8-}$ in $[Cd(NiSn_9)_2]^{6-}$	X-ray (100 K)	3.549	3.011	2.981	5.24	6.71
	DFT ($^1A_{1g}$)	3.71	3.07	3.02	5.32	6.81
$[Sn_{18}]^{6-}$ in $[Fe_3Sn_{18}]^{4-}$	X-ray (100 K)	3.690	3.001	3.004	3.460	4.10
	DFT ($^7A_{2g}$)	3.64	3.07	3.04	3.50	4.22
$[Sn_{18}]^{4-}$ in $[Pd_2Sn_{18}]^{4-}$	X-ray (100 K)	3.268	3.076	3.070	3.272	3.106
	DFT ($^1A_{1g}$)	3.31	3.10	3.13	3.33	3.10

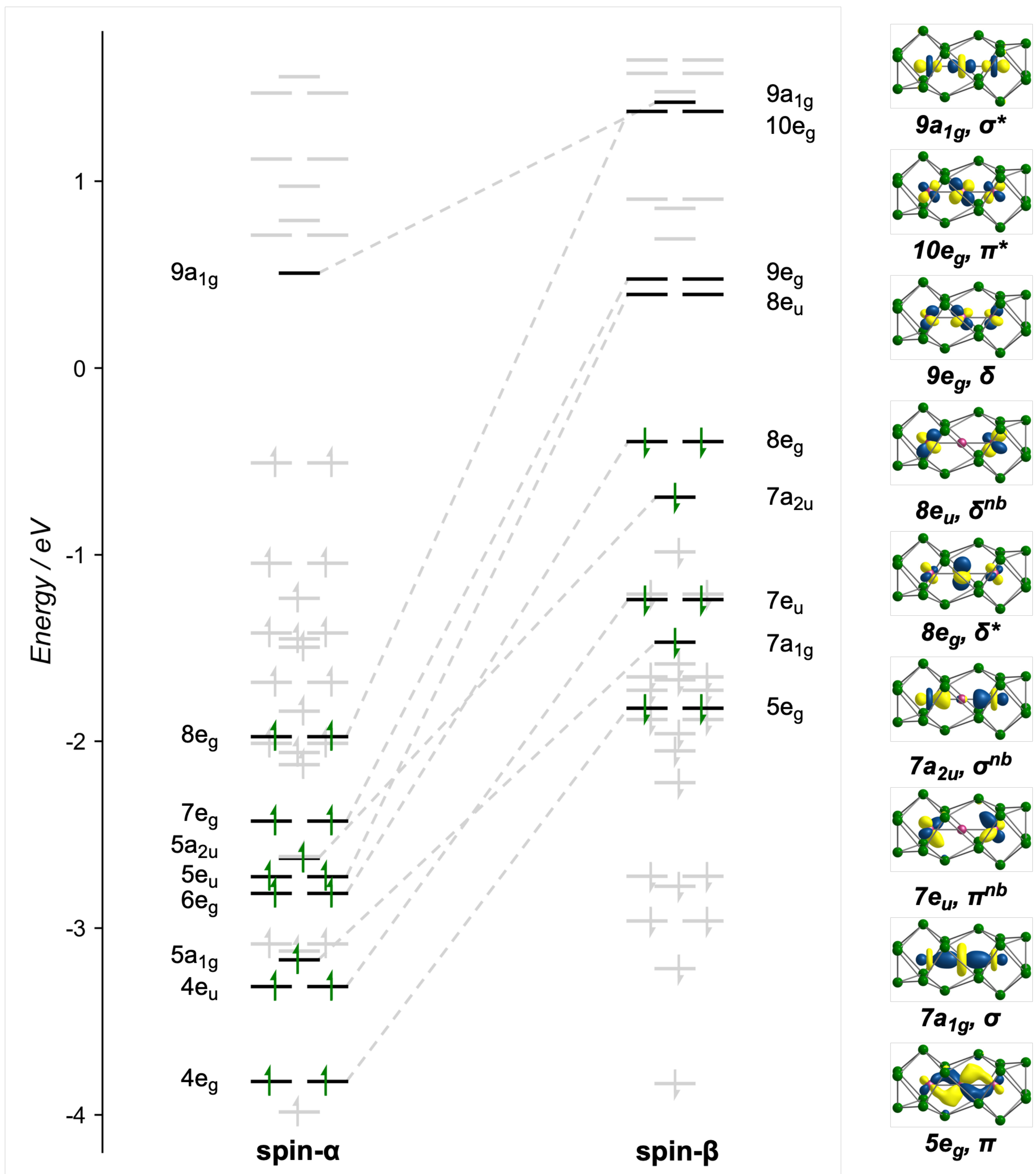
- The Walsh diagram shows the change in orbital energy during the coalescing process. The **7 a_{2u}** (in red) and **7 a_{1g}** (in blue) level are lifted above the Fermi level in a step-wise manner.





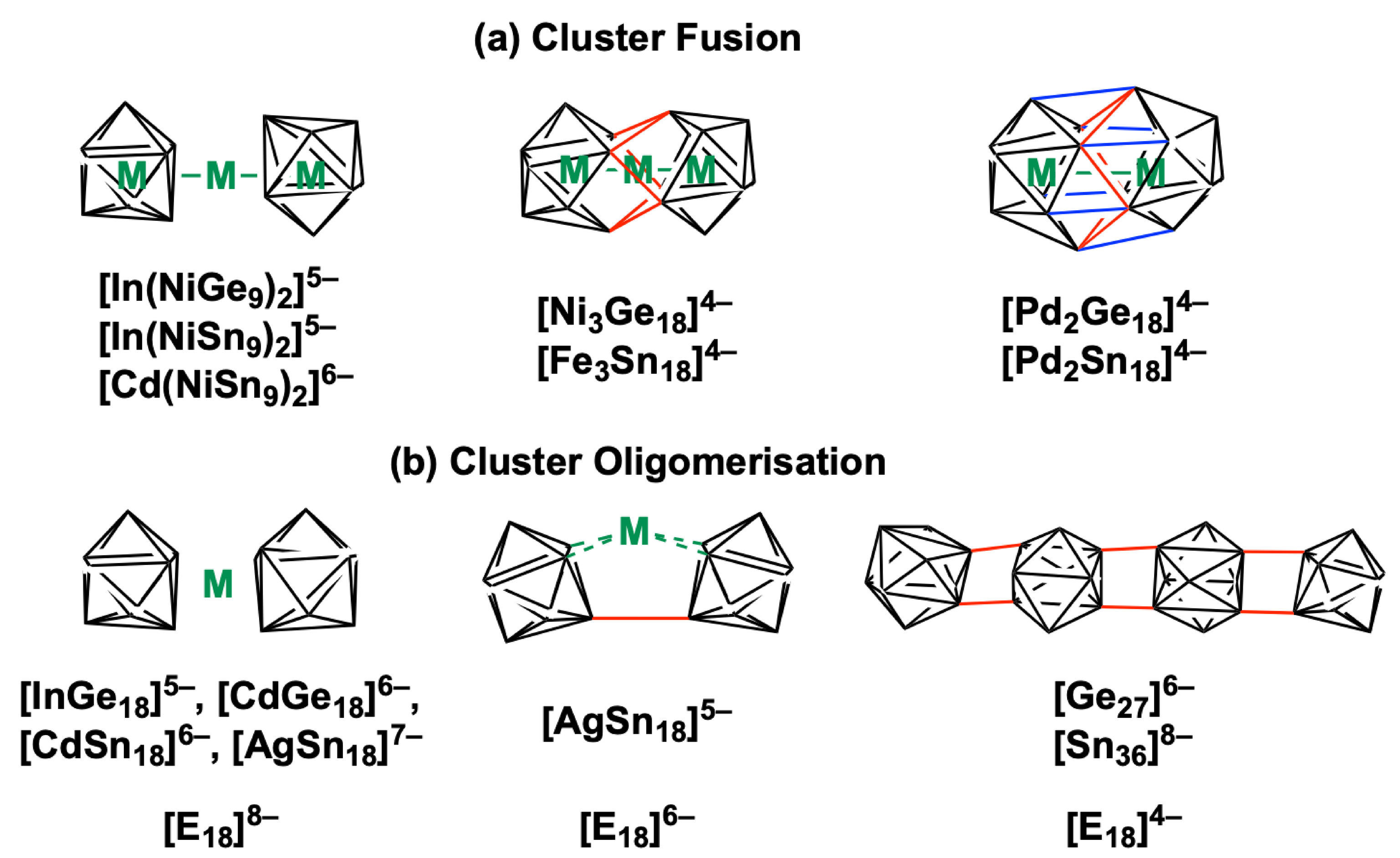
Fe-Fe Bonding Analysis

- A high-spin ground state of **S=3** was identified by DFT. Most spin densities locate on the Fe_3 core, indicating an unfilled Fe 3d shell.
- There are 22 3d electrons distributing among 15 linear combinations of Fe 3d orbitals. The Fe-Fe σ^* orbital is vacant, with the π^* degenerate orbitals appearing singly-occupied. The configurations of the Fe_3 core can be recognized as $\sigma^2\sigma^2_{nb}\sigma^{*0}$ and $\pi^4\pi^{nb4}\pi^{*2}$.
- For each Fe-Fe bond, the composition can be described as $1/2\sigma + 1/2\pi$. The gross bond order is 1, corresponding to the Mayer bond order of 0.95.



Summary and Conclusion

- The reported cluster, $[Fe_3Sn_{18}]^{4-}$, can be regarded as an **intermediate geometry** between the separated-limit and the fused-limit in the cluster coalescence. The **Fe-Fe bonds** are also constructed in this confined space.
- By comparing to existing clusters, we can conclude two pathways of the cluster growth from Sn_9 — **cluster fusion** by forming delocalized bonds between Sn_9 fragments (as $[Fe_3Sn_{18}]^{4-}$) and **cluster oligomerisation** by localized *exo* bond(s) connecting monomers (as $[AgSn_{18}]^{5-}$).



KEY REFERENCES

[1] Z.-S. Li, W.-X. Chen, H. W. T. Morgan, C.-C. Shu, J. E. McGrady and Z.-M. Sun, *Chemical Science*, 2024, **15**, 1018–1026.

[2] Z.-M. Sun, H. Xiao, J. Li and L.-S. Wang, *Journal of the American Chemical Society*, 2007, **129**, 9560–9561.

[3] Y.-N. Yang, L. Qiao and Z.-M. Sun, *Chinese Chemical Letters*, 2023, **34**, 107207.

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MORE INFORMATION

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