

Molecular Aromaticity at the Edge of the Periodic Table

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Abstract: The recent discovery of the cyclically delocalized three-center two-electron σ -bonding in the crystalline actinide cluster isolated by Liddle and co-workers has sparked a heated debate on the role of molecular aromaticity on the periphery of the periodic table. It has been suggested that the tri-thorium ring at the heart of the cluster features considerable aromatic stabilization comparable to the heterocyclic π -aromatic rings such as thiophene. In this Communication we challenge previous conclusions by showing from first principles that the tri-thorium bonding does not fulfill the very fundamental requirement by IUPAC of being distinctly stabilized by cyclic delocalization of electrons, and therefore it should be classified as non-aromatic once and for all.

Introduction

When Kekulé first pictured the ring structure of benzene,[1] hardly anyone could have imagined that electron delocalization and aromaticity may play a central role in an incredible variety of inorganic rings and 3D clusters containing *s*-, *d*- and even *f*-block metal atoms.[2] Very recently, Boronski *et al.* designed and isolated under normal experimental conditions the crystalline actinide cluster $[\{\text{Th}(\eta^8\text{-C}_8\text{H}_8)(\mu_3\text{-Cl})_2\}_3\{\text{K}(\text{THF})_2\}_2]_\infty$ containing at its heart the tri-thorium ring with a pair of uniformly distributed electrons.[3] This discovery has been hailed for extending the range of the aromaticity concept to the record seventh row of the periodic table, and it has been suggested that aromaticity can be an important factor in the design of stable complexes with actinide-actinide bonds (which have previously been reported to be very weak and localized).[4] The follow-up investigations revealed that the experimental data and the results of calculations of the magnetic criteria of aromaticity[5] do not provide solid proves for the existence of the aromatic tri-thorium bond,[6,7] and the unique multicenter charge-shift bonding $(\text{ThCl}_2)_3$ was shown to be the actual factor determining high symmetry (D_{3h}) and exceptional stability of the crystalline actinide cluster.[7] Very recently, Lin and Mo provided further computational data supporting the charge-shift bonding in the actinide cluster, and found that the overall charge transfer between thorium and chlorine atoms is about ten times more stabilizing than electron delocalization in the Th_3 ring.[8] The authors linked the latter with the stabilization effect resulting from the periodic boundary conditions (PBC) for the electron distribution,[9] and made the conclusion that the tri-thorium bonding is therefore “*truly delocalized and σ -aromatic*”.[8] Similar conclusions were drawn by Tomeček *et al.*[10] who utilized the entire arsenal of sophisticated computational methods to demonstrate that the Th_3 ring contains cyclically delocalized electrons and should be regarded σ -aromatic. However, in both works the simplified highly ionized model cluster $\text{Th}_3\text{Cl}_6^{4+}$

was investigated, in which the electron binding energy associated with the highest occupied molecular orbital (HOMO) is incomparably higher in magnitude than in the neutral crystalline cluster. This leads to exaggeration of σ -bonding and charge delocalization between thorium atoms making the conclusions by Lin and Mo,[8] and Tomeček *et al.*[10] not directly transferable to Th₃ in the isolated compound.

In this Communication we demonstrate from first principles that the tri-thorium σ -bonding in the real (neutral) crystalline cluster does not fulfill the fundamental requirement by IUPAC of being distinctly stabilized by cyclic delocalization of electrons compared to the linear isomer,[11] and thus it should be classified as nonaromatic once and for all.

Results and Discussion

To assess the magnitude of aromatic stabilization in the tri-thorium ring, Lin and Mo used the simplified charged model cluster Th₃¹⁰⁺ derived from the Th₃Cl₆⁴⁺ cage at its equilibrium geometry with the highest-occupied molecular orbital (HOMO) that visually resembles the corresponding 3c2e-type HOMO in the original (experimentally validated) model cluster by Boronski *et al.*[3] The authors used a sophisticated computational method called the block-localized wavefunction at the density functional theory (BLW-DFT)[12] to estimate aromatic stabilization in terms of the extra cyclic resonance energy (ECRE). The calculated ECRE value of 18.7 kcal mol⁻¹ (**Figure S1**, Supporting Information) falls between the corresponding values for the archetypical σ -aromatic H₃⁺ (31.9 kcal mol⁻¹) and non-aromatic Li₃⁺ (0.2 kcal mol⁻¹), which prompted Lin and Mo to make the conclusion that the tri-thorium ring is considerably σ -aromatic; for comparison, the aromatic stabilization energy in thiophene is about 18.6 kcal mol⁻¹. [13]

Unfortunately, in addition to several potential issues associated with the very definition of ECRE (see Supporting Information), the conclusion about aromatic stabilization made for such

extremely ionized model cluster as Th_3^{10+} may be not directly transferable to the tri-thorium ring in the isolated compound. This is because strict separation of charge between the Th_3Cl_6 cage and the surrounding ligands in the model crystalline actinide cluster dramatically affects the ECRE in the Th_3 core. Lin and Mo,[8] and Tomeček *et al.*,[10] made the charged model cluster $\text{Th}_3\text{Cl}_6^{4+}$ by removing two K cations (the spectators) and three cyclooctatetraenyl dianion ligands (COT^{2-}) from the original neutral model by Boronski *et al.*[3] However, the covalent bond order[12] between each thorium atom and the corresponding COT ligand is equal to 0.96, which means almost perfect sharing of the $7s^2$ electrons (Th) with the 8π -subsystem (COT) rather than transfer of two electrons to make the aromatic 10π -electron COT^{2-} ligand. To illustrate to what extent separation of charge affects bonding in the core of the actinide cluster, we performed symmetry-constrained relativistic calculations of the $3c2e$ -orbital energy levels in Th_3^{10+} , $\text{Th}_3\text{Cl}_6^{4+}$, Th_3 , and the original model by Boronski *et al.* (Figure 1a).[3] The results clearly show that orbital energies in charged clusters are essentially different from the corresponding orbital energies in the neutral ones. Moreover, the MOs in charged systems are more inhomogeneous due to the significant contribution of the atomic orbitals $7s$ (especially in the Th_3^{10+} model cluster). Also, despite visual similarity between HOMOs in $\text{Th}_3\text{Cl}_6^{4+}$ and the model by Boronski *et al.*, the overlap of three $6d$ orbitals in the former is associated with approximately six times higher electron binding energy, resulting in significantly shorter Th–Th bond length (3.684 Å) compared to the average value from the experiment (3.991 Å).[3] Therefore, it is evident that high ionization level in both charged model clusters result in dramatic exaggeration of σ -bonding, which make them hardly comparable with the experimentally validated neutral model by Boronski *et al.*[3] Consequently, the results of theoretical investigations involving Th_3^{10+} and $\text{Th}_3\text{Cl}_6^{4+}$ cannot be used to justify σ -aromaticity in the isolated crystalline actinide cluster.

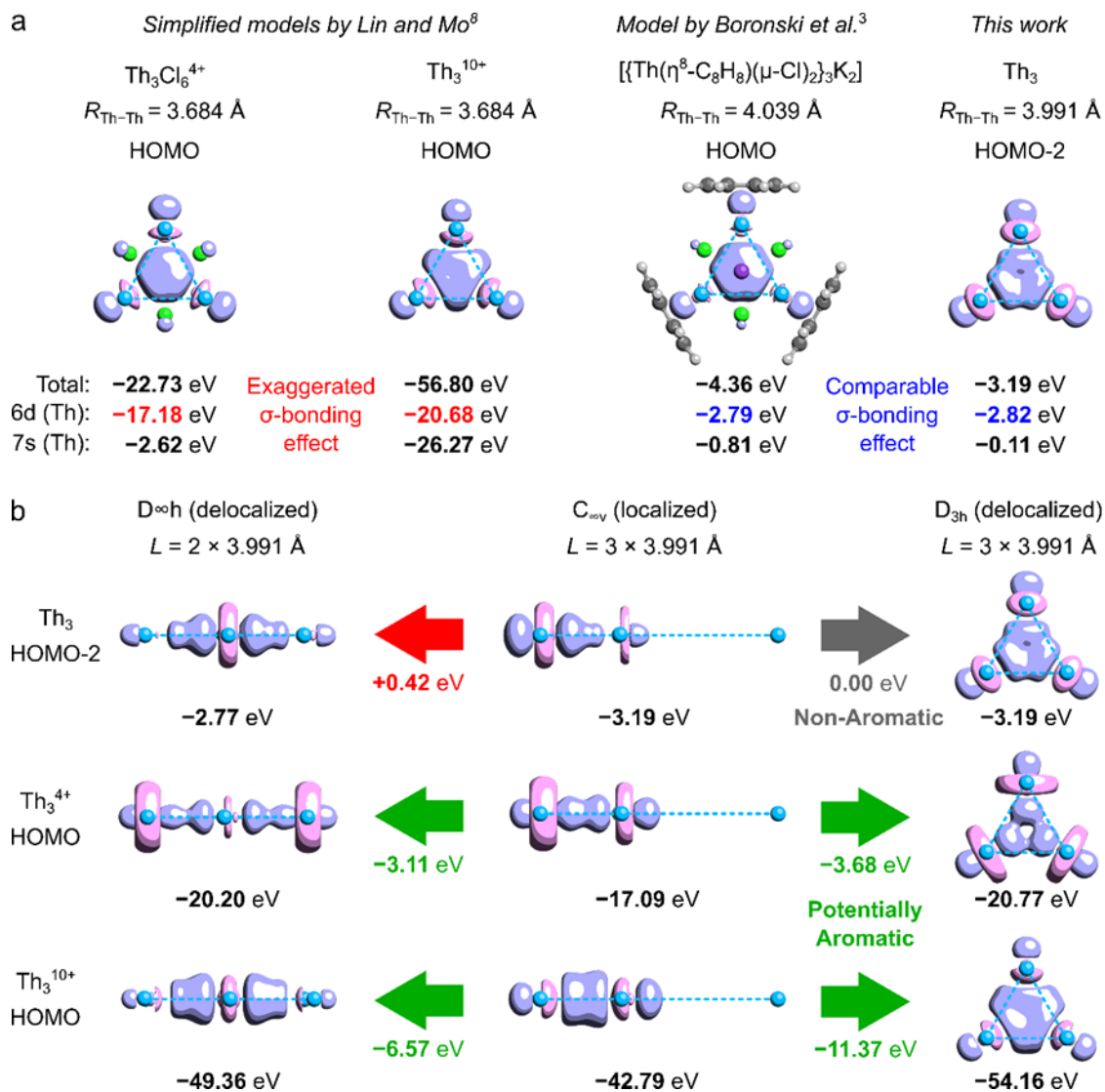


Figure 1. (a) Isosurfaces (visualized at $\tau=0.07e$) of the 3c2e molecular orbitals in selected charged and neutral model tri-thorium clusters with the corresponding total one-electron energies as well as the energy contributions from 6d and 7s atomic orbitals (Th). (b) Comparison of the absolute and relative one-electron orbital energies in selected cyclic and acyclic isomers of the simplified neutral and charged tri-thorium clusters at the experimental geometry ($R_{\text{Th-Th}}=3.991\text{\AA}$). Method: $\omega\text{B97X}/\text{jorge-TZP-DKH}$ with the Douglas-Kroll 2nd-order relativistic Hamiltonian (more details in SI).

To the best of our knowledge, there is no reliable and universal method to quantitatively assess the effect of aromatic stabilization in all-metal clusters. However, in the case of the three-center two-electron bonding the potentially extra stabilizing effect of PBC can be deduced from the molecular orbital energies in linear and cyclic isomers. This is because within the one-electron approximation the effect of the periodic boundary conditions on the 3c2e σ -bonding is directly proportional to the corresponding effect on the 3c2e orbital itself (**Figure S3**, SI). Accordingly, by comparison of the orbital energy levels of the equal-length linear asymmetric ($C_{\infty v}$) and cyclic symmetric (D_{3h}) forms of the models Th_3 , Th_3^{4+} , and Th_3^{10+} , it can easily be found that only in the ionized clusters the D_{3h} isomers (with cyclically delocalized charge) have the orbital energies lower than the $C_{\infty v}$ isomers (with the electrons shared only by two Th atoms) (**Figure 2b**). This means that only the charged model clusters can be considered effectively stabilized by the PBC. Contrariwise, in the neutral model Th_3 the corresponding 3c2e orbital in the cyclic isomer clearly makes no profits from the PBC as it has exactly the same orbital energy as its linear asymmetric counterpart (with more localized charge). It should be noted that the energy differences between isomers $C_{\infty v}$ and D_{3h} (0.00 eV, -3.68 eV, and -11.37 eV) correlate linearly ($R^2 = 0.993$) with the corresponding total charges of the model tri-thorium clusters (0, +4, +10), while the lack of such correlation is observed for the orbital energy differences between isomers $D_{\infty h}$ and D_{3h} . This is a direct manifestation of the foregoing incompatibility of these isomers (in the context of the PBC effect)[10] due to different total lengths, L . Nevertheless, the fact that the $C_{\infty v}$ isomer has lower orbital energy than the contracted $D_{\infty h}$ one (with more extended charge delocalization) clearly shows that the atomic orbitals 6d are rather reluctant to σ -conjugation at this distance. This, in turn, is in full agreement with the conclusions from our previous study based on the analysis of the topological characteristics of the electron density.[7]

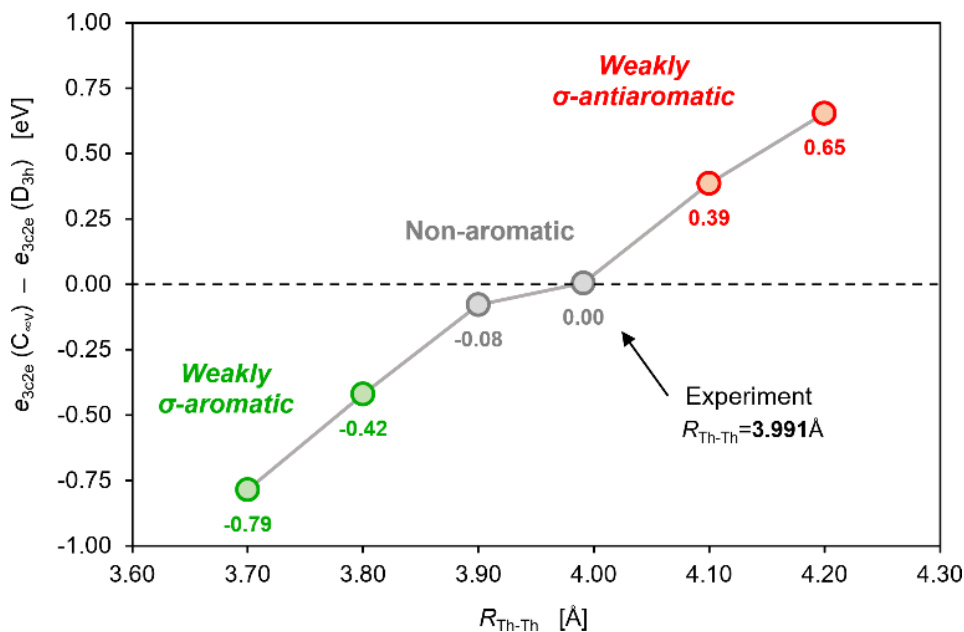


Figure 2. The stabilizing and destabilizing effects of the periodic boundary conditions on the three-center two-electron σ -bonding in the neutral model cluster Th_3 at different bond lengths, $R_{\text{Th-Th}}$.

It should be noted that at distance shorter than the experimental one ($R_{\text{Th-Th}}=3.991 \text{ \AA}$) the overlapping of 6d orbitals in the neutral tri-thorium ring may be much more effective, and weak but noticeable σ -aromatic stabilization could be theoretically possible (**Figure 2**). However, one must realize that even a small contraction of Th–Th bonds in the crystalline actinide cluster implies size reduction of the entire Th_3Cl_6 cage, and consequently the enhancement of the Pauli repulsion between lone pairs of chlorine atoms crowded in the relatively small volume. This has been argued to have a negative impact on the thermodynamic stability of the complex.[7] Therefore, the strong multicenter charge-shift bonding in the Th_3Cl_6 cage seems to enlarge the ring of weakly bonded thorium atoms inside to the extent that prevents any extra cyclic stabilization. This puts into question the core-shell syngenetic model of aromaticity proposed by Lin and Mo.[8]

Conclusions

The crystalline actinide cluster isolated by Boronski *et al.* represents an interesting and important case in which the cyclic delocalization of electrons inside the all-metal core is not associated with aromatic stabilization, but is dictated by the symmetry of the network of the surrounding bonds.[7] In fact, the charge transfer between thorium and chlorine atoms makes the multicenter charge-shift bonding in the Th_3Cl_6 cage particularly strong, but at the same time it impairs the direct σ -bonding of Th atoms to the extent in which the Th_3 ring (D_{3h}) exhibits no extra stabilization compared to its linear and more localized isomer ($C_{\infty v}$). Thus, in accordance with the very first sentence of the recommendation by IUPAC (*'Aromaticity is the concept of spatial and electronic structure of cyclic molecular systems displaying the effects of cyclic electron delocalization which provide for their enhanced thermodynamic stability relative to acyclic structural analogues (...)'*),[11] the tri-thorium ring cannot be classified as σ -aromatic. The results presented in this and previous studies suggest that actinide atoms are simply too heavy (with the valence electrons bonded too weakly) to form strong covalent σ -bonds with their 6d orbitals, and consequently the superposition of the resonance forms containing such bonds is expected to bring rather marginal extra stabilization to the system, if any. This fact may have broader implications for not only clarifying the limits of aromaticity on the periphery of the periodic table, but also for understanding the chemistry of actinides and future attempts to design and synthesize stable actinide complexes. Finally, the presented results demonstrate that the aromatic stabilization effect in small rings increases almost linearly with the ionization level. Consequently, the results of previous theoretical investigations involving ionized model clusters like Th_3^{10+} and $\text{Th}_3\text{Cl}_6^{4+}$ cannot be used to justify aromaticity in the crystalline cluster isolated by Boronski *et al.*[3]

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References

- [1] A. Robinson, Chemistry's visual origins, *Nature* 465 (2010) 36–36. <https://doi.org/10.1038/465036a>.
- [2] J. M. Mercero, A. I. Boldyrev, G. Merino, J. M. Ugalde, Recent developments and future prospects of all-metal aromatic compounds, *Chem. Soc. Rev.* 44 (2015) 6519–6534. <https://doi.org/10.1039/C5CS00341E>.
- [3] J. T. Boronski, J. A. Seed, D. Hunger, A. W. Woodward, J. van Slageren, A. J. Wooles, L. S. Natrajan, N. Kaltsoyannis, S. T. Liddle, A crystalline tri-thorium cluster with σ -aromatic metal–metal bonding, *Nature* 598 (2021) 72–75. <https://doi.org/10.1038/s41586-021-03888-3>.
- [4] T. Cheisson, K. D. Kersey, N. Mahieu, A. McSkimming, M. R. Gau, P. J. Carroll, E. J. Schelter, Multiple Bonding in Lanthanides and Actinides: Direct Comparison of Covalency in Thorium(IV)- and Cerium(IV)-Imido Complexes, *J. Am. Chem. Soc.* 141 (2019) 9185–9190. <https://doi.org/10.1021/jacs.9b04061>.
- [5] R. Gershoni-Poranne, A. Stanger, Magnetic criteria of aromaticity, *Chem. Soc. Rev.* 44 (2015) 6597–6615. <https://doi.org/10.1039/C5CS00114E>.
- [6] A. B. J. Cuyacot, C. Foroutan-Nejad, [$\text{Th}(\text{C}_8\text{H}_8)\text{Cl}_2$] $_3$ $^{2-}$ is stable but not aromatic, *Nature* 603 (2022) E18–E20. <https://doi.org/10.1038/s41586-021-04319-z>.

- [7] D. W. Szczepanik, 2022. Bonding in a Crystalline Tri-Thorium Cluster: Not σ -Aromatic But Still Unique. *Angew. Chem. Int. Ed.* 61, e202204337. <https://doi.org/10.1002/anie.202204337>.
- [8] X. Lin, Y. Mo, 2022. On the Bonding Nature in the Crystalline Tri-Thorium Cluster: Core-Shell Syngenetic σ -Aromaticity. *Angew. Chem. Int. Ed.* 61, e202209658. <https://doi.org/10.1002/anie.202209658>.
- [9] M. Solà, F. M. Bickelhaupt, Particle on a Ring Model for Teaching the Origin of the Aromatic Stabilization Energy and the Hückel and Baird Rules, *J. Chem. Educ.* 99 (2022) 3497–3501. <https://doi.org/10.1021/acs.jchemed.2c00523>.
- [10] J. Tomeček, S. T. Liddle, N. Kaltsoyannis, 2023. Actinide-Actinide Bonding: Electron Delocalisation and σ -Aromaticity in the Tri-Thorium Cluster [$\{\text{Th}(\eta^8\text{-C}_8\text{H}_8)(\mu\text{-Cl})_2\}_3\text{K}_2$]. *ChemPhysChem* 24, e202300366. [10.1002/cphc.202300366](https://doi.org/10.1002/cphc.202300366).
- [11] V. I. Minkin, Glossary of terms used in theoretical organic chemistry, *Pure Appl. Chem.* 71 (1999) 1919–1981. <http://dx.doi.org/10.1351/pac199971101919>.
- [12] Y. Mo, L. Song, Y. Lin, Block-Localized Wavefunction (BLW) Method at the Density Functional Theory (DFT) Level, *J. Phys. Chem. A* 111 (2007) 8291–8301. <https://doi.org/10.1021/jp0724065>.
- [13] K. Najmidin, A. Kerim, P. Abdirishit, H. Kalam, T. Tawar, A comparative study of the aromaticity of pyrrole, furan, thiophene, and their aza-derivatives., *J. Mol. Model.* 19 (2013) 3529–3535. <https://doi.org/10.1007/s00894-013-1877-x>.
- [14] D.W. Szczepanik, J. Mrozek, On quadratic bond-order decomposition within molecular orbital space, *J. Math. Chem.* 51 (2013) 1619–1633. <https://doi.org/10.1007/s10910-013-0169-0>.