A Crystalline Tri-thorium Cluster: When Metal σ-Aromaticity Just Isn't Enough

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When Kekulé first pictured the ring structure of benzene,[1] hardly anyone could have imagined that aromaticity may play a central role in an incredible variety of organic and inorganic rings containing *s*-, *d*- and even *f*-block metal atoms.[2] Very recently, Liddle and coworkers extended the range of aromaticity to a record seventh row of the periodic table by successful isolation of the crystalline actinide cluster $[\{Th(\eta^8\text{-}C_8H_8)(\mu_3\text{-}Cl)_2\}_3\{K(THF)_2\}_2]_\infty$ (**3**) containing at its heart the three-membered σ-aromatic ring built exclusively from thorium atoms.[3] Unfortunately, the authors have misinterpreted one the key evidences for the existence of the σ-aromatic tri-thorium bonding and overlooked several important factors that put into question the main conclusion of the original article in Nature that "*the experimental discovery of actinide σ-aromatic bonding (...) constitutes a new approach to elaborating actinide-actinide bonding*".[3]

In the following, we challenge the conclusion above by a thorough reexamination of the molecular properties of the simplified model of **3**, $[\{Th(\eta^8\text{-}C_8H_8)(\mu\text{-}Cl)_2\}_3K_2]$ (**3**''), originally designed by the authors and used to interpret the experimental Raman spectrum of **3**.[3] Studying the broad inelastic scattering bands between 60 and 160 cm^{-1}, Liddle *et al.* assigned the corresponding peaks in **3**'' exclusively to the asymmetric Th–Th stretching (73 cm^{-1}) and symmetric breathing modes (78 and 107 cm^{-1}). However, a closer inspection of each of these vibration modes reveals that the displacements of the thorium and chlorine atoms have comparable amplitudes (**Figure 1a**), and therefore should be interpreted as collective symmetric and asymmetric stretching (Th–Cl) and bending (Th–Cl–Th and Cl–Th–Cl) vibrations within the entire Th_3Cl_6 cage, rather than the sole stretching in the Th_3 core (**Table S1** and the corresponding video files). Furthermore, going beyond 160 cm^{-1}, we can easily find asymmetric Th–Cl stretching (e.g., at 192 cm^{-1}) and all sorts of bending modes that involve all the atoms in the Th_3Cl_6 cage. Many of them, such as the asymmetric bending at 214 cm^{-1}, are detectable in the

Raman spectrum of **3**” (due to weakly bonding and easily polarizable density of delocalized electrons in the σ-aromatic Th_3 ring), but also in the infrared (IR) spectrum, strongly suggesting the presence of highly polarized covalent bonds Th–Cl (**Table S1**).

It should also be noticed that the covalent bond orders calculated by the authors (0.251 for Th–Th and 0.374 for Th–Cl) in themselves signify the potential importance of the thorium-chlorine bonds, especially when we consider that within the Th_3Cl_6 cage there is formally four times more the Th–Cl than the Th–Th bonds. Therefore, it seems that by focusing too narrowly on the Th_3 bonding in **3**, the authors may have oversold the importance of σ-aromaticity and, at the same time, overlooked the unique thorium-chlorine bonding pattern that can be essential for understanding the electronic structure of the synthesized crystalline cluster and its stability.

To even better illustrate the issue and highlight the actual role of tri-thorium bonding, in the following we compare the σ-aromatic model **3**” with its non-aromatic counterpart, $[\{Th(\eta^8\text{-}C_8H_8)(\mu\text{-}Cl)_2\}_3Ar_2]$ (**3***), in which potassium atoms are replaced by argon atoms, thus removing two delocalized electrons from the Th_3 ring. Although there is no direct bonding between thorium atoms in **3***, the non-aromatic cluster shares most of the structural (**Figure S1**), molecular-orbital (**Figure S2**), and thermodynamic features of **3**” (**Figure 1b**), except the magnetic-response properties (**Figure S3**). It should be noted that the infrared (IR) spectra of both model clusters show a large overlap (**Figure 1b**), and the corresponding molecular vibration contributions to the thermal energy differ by less than 1 kcal mol^{-1}, indicating a marginal effect of the σ-aromatic tri-thorium bonding on the thermodynamic stability of **3**”. Interestingly, a careful comparison of molecular vibrations within the Th_3Cl_6 cage in **3**” and **3*** reveals that the most characteristic modes (except 107 cm^{-1}) feature both the σ-aromatic and non-aromatic cluster, although in the latter they are hardly detectable in Raman spectroscopy (**Figure 1a** and

Table S1). This simple fact proves incontrovertibly that the original assignment of the vibration modes between 60 and 160 cm^{-1} exclusively to the Th–Th stretching was certainly inaccurate.[3]

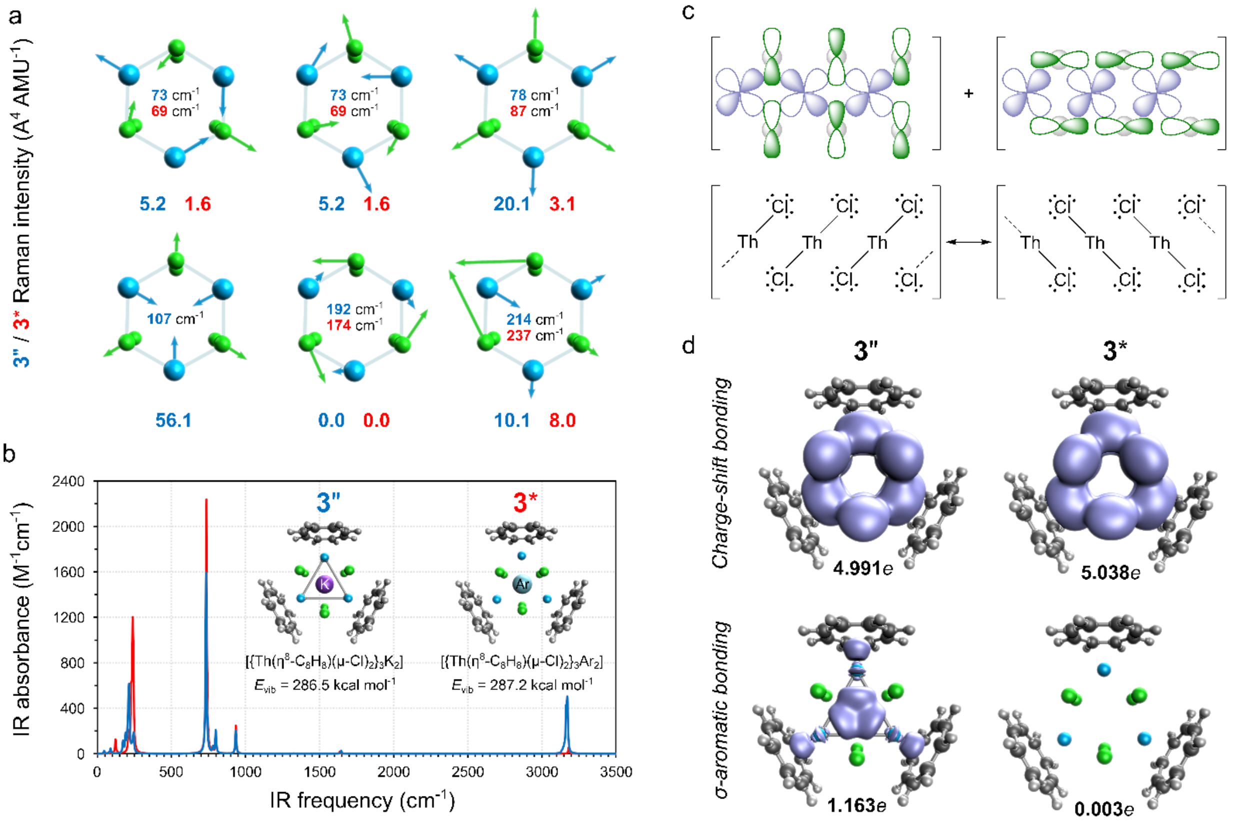

Figure 1. (a) Selected molecular vibration modes in **3**" with the corresponding frequencies inscribed inside the Th_3Cl_6 cage and the Raman intensities given below; blue and red numbers refer to the model clusters **3**" and **3***, respectively. (b) The IR spectra of **3"** and **3*** with the corresponding molecular vibration contributions to the thermal energy. (c) Linearized side-view of two orbital conjugation topologies in which the overlapping of the 6d (Th) and 3p (Cl) orbitals is particularly effective; below, the associated resonance Lewis structures. (d) Isosurfaces (at τ = 0.003*e*) of the EDDB function dissected into contributions to the resonance stabilization from the charge-shift bonding and the σ-aromatic bonding; the bold numbers below the structures represent the populations of the electron pairs 'resonating' between different bond positions.

To elucidate the nature of bonding within the Th_3Cl_6 cage, we analyzed possible conjugation topologies of the atomic orbitals 6d (thorium) and 3p (chlorine) and found two configurations in which the in-phase orbital overlap is expected to be particularly effective (**Figure 1c**). The superposition of these orbital configurations enables a unique resonance mode with polarized thorium-chlorine and the corresponding dative bonds cooperatively switching their positions; this type of bond is known in the literature as a charge-shift bond.[4,5] In fact, additional high-level relativistic calculations reveal that within the Th_3Cl_6 cage thorium and chlorine atoms act as divalent and monovalent elements, respectively, and the formal bond-order of Th–Cl is 0.5 (see **Supporting Information** for more details), which perfectly corresponds to the proposed resonance Lewis structures (**Figure 1c**) and fully confirms that Liddle *et al.* unwittingly discovered a new type of the actinide-halogen bonding, that is, the multicenter charge-shift bond Th_3Cl_6. To assess the magnitude of this unique bond, we used the state-of-the-art method called the Electron Density of Delocalized Bonds (EDDB),[6] which ‘extracts’ from the molecular wavefunction the density of the electron pairs resonating between different bond positions, providing a unique tool to visualize and quantify any kind of the resonance-stabilized bonding from typical π-aromatics to weak anagostic interactions.[6] The results of the EDDB analysis show a clear and distinct picture of two different types of the resonance-stabilization effects in the Th_3Cl_6 cage (**Figure 1d**): the multicenter charge-shift bonding with the total population of 5.0*e* effectively resonating over the thorium-chlorine bond positions, and the weak σ-aromatic tri-thorium bonding, in which only about 1.2*e* can be associated with the stabilizing character. Therefore, from the resonance electronic-structure perspective, the multicenter charge-shift bonding is about four times more effective at stabilizing **3**” than the σ-aromaticity. Furthermore, the multicenter charge-shift bonding remains almost unchanged even without the presence of the σ-aromatic Th_3 bonding in **3***, which perfectly corresponds to the structural, thermodynamic, and spectral similarities between **3**” and **3***, and therefore ultimately downplays the importance of actinide σ-aromaticity in **3**.

To conclude, in this study we proved that Liddle and coworkers have misinterpreted the experimental Raman spectrum of **3**, which eventually led to the wrong conclusions about the role of the σ-aromatic tri-thorium bonding in the synthesized and isolated crystalline actinide cluster. We demonstrated that the thorium-thorium bond in **3** is not very different from the already known extremely weak actinide-actinide bonds,[7] and the marginal σ-aromatic stabilization in the Th_3 ring makes it hardly distinguishable from ordinary non-aromatic rings. Also, we showed that the multicenter charge-shift bonding in the Th_3Cl_6 cage is a vital factor that determines the uniqueness and remarkable thermodynamic stability of **3**. The charge-shift bonds have recently been shown to be particularly strong when the 5d orbitals of the transition-metals from group 11 and 12 are involved,[8] but this study extends the range of the charge-shift bonding beyond transition metals to the seventh row of the periodic table.

By clarifying the misleading conclusions of the original Nature paper[3] and drawing special attention to the essential stabilizing role of actinide-halogen charge-shift bonding, this study may have broader implications for understanding the chemistry of actinides and future attempts to design and synthesize new stable actinide complexes.

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Data availability

Supporting Information contains details of computational methods and analyses employed to perform the present work, a brief discussion of the aromatic character of the tri-thorium bonding (critically addressing the recent findings questioning σ-aromaticity in **3**”),[9] **Table S1** and **Figures S1-4**, the optimized XYZ coordinates, and video files visualizing the results of the vibration analyses of **3**” and **3***.

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