A σ-Aromatic Tri-Thorium Bonding: Does It Really Exist?

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The experimental realization of actinide-actinide bonding in isolable molecules has been one of the main targets of synthetic actinide chemistry for decades[1,2]. Very recently, Boronski *et al.* reported the first thorium-thorium bonding in a crystalline cluster prepared and isolated under normal experimental conditions, $[\{Th(\eta^8-C_8H_8)(\mu_3-Cl)_2\}_3\{K(THF)_2\}_2]_\infty$ (**3**)[3]. The electron spin resonance and the superconducting quantum-interference device magnetometry revealed a diamagnetic ground-state with two electrons equally distributed over the tri-thorium ring at the heart of **3**, and the recorded Raman spectrum allegedly confirmed the existence of a three-center two-electron (3c-2e) bond. However, the broad inelastic scattering bands centered at 72 and 105 cm^{-1}, originally assigned by the authors to Th–Th vibrations, represent in fact the combination of Th–Cl stretching and Cl–Th–Cl bending, and as demonstrated in the following, they establish the existence of a unique charge-shift actinide-halogen bonding rather than the σ-aromatic (delocalized) actinide-actinide bonding as claimed in the original article[3].

To understand the electronic structure of **3**, Boronski *et al.* computationally investigated several model clusters, including $[\{Th(\eta^8-C_8H_8)(\mu-Cl)_2\}_3K_2]$ (**3"**) with the Highest Occupied Molecular Orbital (HOMO) reminiscent of a 3c-2e bond, and its dication $[\{Th(\eta^8-C_8H_8)(\mu-Cl)_2\}_3K_2]^{2+}$ (here denoted by **3***) without the characteristic 3c-2e HOMO. The authors found that the structure of **3"** better fits the X-ray diffraction data and the calculated vibration modes match well with the intensive signals observed in the experimental Raman spectrum, which they interpreted as an "*experimental confirmation of the Th₃ bonding in 3*". However, such an interpretation is mostly inaccurate as the same vibration modes feature the model cluster **3***, which lacks any direct actinide-actinide bonding (the reported thorium-thorium bond orders for **3"** and **3*** are 0.254 and 0.039, respectively). As shown in **Figure 1a** (and in the Supplementary Video clip), the symmetric breathing modes centered at 77 and 107 cm^{-1} in **3"** can easily be

found respectively at 75 and 103 cm^{-1} in **3***, although the lack of delocalized and highly polarizable HOMO in the latter makes them hardly detectable in Raman spectroscopy. Furthermore, the authors overlooked the fact that the displacement vectors on thorium and chlorine atoms in both model clusters have comparable magnitudes, which strongly suggests that the observed broad inelastic scattering bands between 60 and 135 cm^{-1} represent collective stretching and bending modes of the actinide-halogen rather than actinide-actinide bonding. This becomes particularly evident if one compares the overall bond order in the tri-thorium ring in **3"**, $3 \times 0.254 = 0.762$, with twelve polarized thorium-chlorine bonds, $12 \times 0.599 = 7.188$ (here the full bond order of 0.599 is the sum of the reported by the authors covalent bond order of 0.374 and the ionic component estimated from the modified Evarestov-Veryazov equation[4], 0.225). These numbers clearly show that more than 90% of bonding interactions in the entire Th$_3$Cl$_6$ cage in the model cluster **3"** are associated with the thorium-chlorine bonds (for **3*** it is 99%), which actually explains the very small frequency shifts between the corresponding symmetric vibration modes in **3"** and **3***. It should also be noticed that the overall vibrational contributions to thermal energy in **3"** (286.5kcal mol^{-1}) and **3*** (287.3 kcal mol^{-1}) differ by less than 1 kcal mol^{-1}, which further confirms extremely weak tri-thorium bonding (if any) and its marginal effect on the thermodynamic stability of **3**.
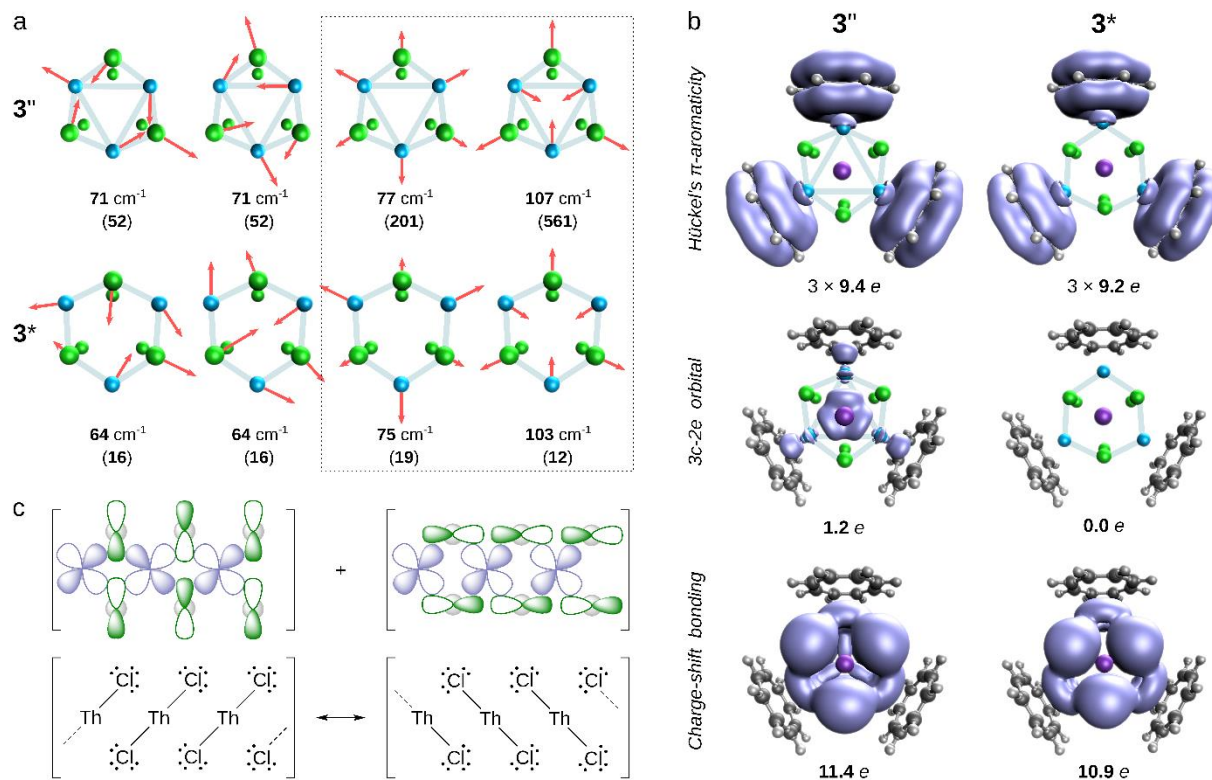
Figure 1. (a) Selected molecular vibration modes in **3"** and **3*** with the corresponding Raman scattering activities in brackets (in units A^4AMU^{-1}). (b) Isosurfaces (at $0.003e$) of the EDDB function in **3"** and **3*** dissected into separate contributions to global electron delocalization from the $C_8H_8^{2-}$ ligands, Th_3 ring, and the entire Th_3Cl_6 cage (with the Th_3 delocalization excluded). (c) The linearized side-view of two orbital conjugation topologies in which the overlap of the 6d (Th) and 3p (Cl) atomic orbitals is expected to be particularly effective; below the corresponding resonance Lewis structures that rationalize the delocalized ("resonating") nature of the thorium-chlorine bonding in the Th_3Cl_6 cage in **3"** and **3***.

In the light of the above clarification, the existence of the tri-thorium bonding in the synthetized crystalline actinide cluster remains experimentally unproven. Going further, the uniform charge distribution over the tri-thorium ring in **3"** is evidently forced by highly symmetric (D_{3h}) arrangement of the thorium-chlorine bonds in the Th_3Cl_6 cage, and as such it may have nothing to do with the aromatic stabilization effect. In this context, negative values of the nucleus-independent chemical shift (NICS)[5] reported by the authors are meaningless as NICS is unable to distinguish between the magnetic shielding caused by the aromatic ring current and

the local circulations around the lone-pairs on the surrounding chlorine atoms[6]. This is a well-known issue of NICS, and for this reason the quantities based on electron density are much more reliable probes of aromaticity in the metal clusters[7]. For instance, the electron density of delocalized bonds (EDDB)[8], presented in **Figure 1b**, provides very clear and distinct pictures of electron delocalization in **3"** and **3*** that fully confirm the dominating role of the delocalized thorium-chlorine bonding in the Th_3Cl_6 cage, which is comparable in magnitude to the cyclic delocalization in the π-aromatic $C_8H_8^{2-}$ ligands, and an order of magnitude higher than in Th_3.

As shown in **Figure 1c**, the delocalized nature of the Th_3Cl_6 bonding can easily be rationalized on the ground of the chemical resonance theory: the polarized bonds Th–Cl and the corresponding lone-pairs on chlorine atoms cooperatively switch their positions giving rise to the formal half-bonding between thorium and chlorine atoms, which is fully consistent with the estimated above full bond order of Th–Cl (0.599). This type of bonding is known in the literature as a charge-shift bond,[9,10] and it has recently been shown to be particularly strong when 5d orbitals of the transition-metals from groups 11 and 12 are involved.[11] Therefore, the unwittingly discovered by Boronsky *et al.* delocalized actinide-halogen bonding pattern extends the range of the charge-shift bonding beyond transition metals to the seventh row of the periodic table.

To summarize, by clarifying inaccurate and misleading conclusions of the original Nature paper[3] and drawing special attention to the essential 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.

Data Availability

All the data investigated within this paper come from the original paper by Boronsky *et al.*[3] or were calculated using the same methodology, computational level and the quantum-chemical

software. The supplementary video clip visualizes the symmetric vibration modes at 77 and 107 cm^{-1} in **3”** (left column), and the corresponding modes at 75 and 103 cm^{-1} in **3*** (right column). The results of the bond order and electron delocalization analyses were validated in the fully relativistic Douglas-Kroll-Hess 4th-order calculations (including the spin-orbit coupling terms and the fully relativistic basis set of the triple-zeta quality), and the resulting data are available from the corresponding author upon reasonable request.

References

1. Cavigliasso, G., Kaltsoyannis, N. On the paucity of molecular actinide complexes with unsupported metal-metal bonds: a comparative investigation of the electronic structure and metal-metal bonding in U_2X_6 (X = Cl, F, OH, NH_2, CH_3) complexes and d-block analogues. *Inorg. Chem.* **45**, 6828‑6839 (2006).

2. Huh, D. N., Roy, S., Ziller, J. W., Furche, F. & Evans, W. J. Isolation of a square-planar Th(III) complex: synthesis and structure of $[Th(OC_6H_2{}^tBu_2\text{-}2,6\text{-}Me\text{-}4)_4]^{1-}$. *J. Am. Chem. Soc.* **141**, 12458‑12463 (2019).

3. Boronski, J.T., Seed, J.A., Hunger, D., Woodward A.W., van Slageren J., Wooles A.J., L.S. Natrajan, Kaltsoyannis N., Liddle S.T. A crystalline tri-thorium cluster with σ-aromatic metal–metal bonding. *Nature* **598**, 72–75 (2021).

4. Szczepanik, D.W., Mrozek, J. Probing the interplay between multiplicity and ionicity of the chemical bond. *J. Theor. Comput. Chem.* **10**, 471−482 (2011).

5. Chen, Z., Wannere, C. S., Corminboeuf, C., Puchta, R., Schleyer, P. von R. Nucleus-Independent Chemical Shifts (NICS) as an Aromaticity Criterion. *Chem. Rev.* **105**, 3842–3888 (2005).

6. Cuyacot, A.B.J., Foroutan-Nejad, C. Aromatic, or Antiaromatic, That Is the Question. Preprint at http://doi.org/10.33774/chemrxiv-2021-3gv6v (2021).

7. Feixas, F., Jiménez-Halla, J.O.C., Matito, E., Poater, J., Solà, M. A test to evaluate the performance of aromaticity descriptors in all-metal and semimetal clusters. An appraisal of electronic and magnetic indicators of aromaticity. *J. Chem. Theory Comput.* **6**, 1118–1130 (2010).

8. Szczepanik, D.W., Andrzejak, M., Dyduch, K., Zak, E.J., Makowski, M., Mazur, G., Mrozek, J. A uniform approach to the description of multicenter bonding. *Phys. Chem. Chem. Phys.* **16**, 20514−20523 (2014).

9. Shaik, S., Danovich, D., Wu, W., Hiberty, P.C. Charge-shift bonding and its manifestations in chemistry. *Nature Chem.* **1**, 443–449 (2009).

10. Shaik, S., Danovich, D., Galbraith, J.M., Braïda, B., Wu, W., Hiberty, P.C. Charge-shift bonding: a new and unique form of bonding. *Angew. Chem. Int. Ed.* **59**, 984–1001 (2020).

11. Joy, J., Danovich, D., Kaupp, M., Shaik, S., Covalent vs Charge-Shift Nature of the Metal–Metal Bond in Transition Metal Complexes: A Unified Understanding. *J. Am. Chem. Soc.* **142**, 12277–12287 (2020).