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Surprising Coordination for Low-Valent Actinides Resembling Uranyl(VI) in Thorium(IV) Organic Hybrid Layered and Framework Structures Based on a Graphene-Like (6,3) Sheet Topology

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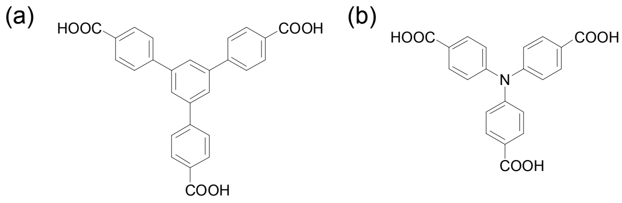
Three thorium(IV)-based metal-organic hybrid compounds with 2D layered and 3D framework structures exhibiting graphene-like (6,3) sheet topologies were prepared with linkers with threefold symmetry. These compounds contain rare and relatively anisotropic coordination environments for low-valent actinides that are similar to those often observed for high-valent actinide ions.

A detailed understanding of the coordination chemistry of actinides is critical for all aspects of modern nuclear fuel cycles including uranium mining,[1] nuclear fuel processing,[2] spent fuel partitioning,[3] waste form design for geological disposals,[4] and predicting the fate and remediation of radionuclides in the environment.[5] The chemistry of actinides is significantly more complex than their lanthanide counterparts, which stems in part from a multitude of available oxidation states and corresponding changes in coordination environments.[6] Typically, actinides with penta- or hexavalent oxidation states are found within linear dioxo actinyl cations $[AnO_2]^{+/2+}$ (An = U, Np, Pu, Am), where further coordination mostly occurs in the equatorial plane, affording tetragonal, pentagonal, and hexagonal bipyramidal coordination geometries.[7] Owing to the inert nature of the uranyl dioxo atoms, these bipyramids condense to predominately form 2D layered structures, in fact, approximately 85% of uranyl(VI) inorganic compounds adopt layered configuration.[7] Whereas low-valent (III, IV) actinides exhibit similar coordination chemistry with that of lanthanides, whose coordination geometries are often isotropic, and seem to be based primarily on ligand repulsion, leading to 3D framework structure types. As a result, the chemical behaviour of high-valent and low-valent actinides are substantially different under a variety of conditions.[6]

We recently reported two unique uranyl(VI)-based metal organic hybrid compounds with large conjugated polycarboxylate ligands, one of which exhibits honey-comb layered structures with a graphene-like (6,3) sheet topology originating from hexagonal bipyramidal geometry of U(VI). The second compound represents the first case of a 2D+2D→3D uranyl polycatenated framework based on the same sheet topology.[8] These compounds show remarkable radiation damage resistance and chemical stability in aqueous media, and are able to selectively capture cesium ions from aqueous solutions without structural degradation.[8] In an effort to expand this type of coordination chemistry to Th(IV) as a representative low-valent actinide ions, three Th(IV)-based metal organic hybrid compounds, namely $[C_7H_{11}N_2]_5[Th_2(L1)_2Cl_6]\cdot Cl$ (**1**), $[C_7H_{11}N_2]_2[Th(L1)Cl_3]$ (**2**), $[(CH_3)_2NH_2][Th_2(L2)_3(H_2O)_2]\cdot 8H_2O\cdot 6DMF$ (**3**), have been synthesized either from solvothermal or ionothermal reactions (see ESI). Surprisingly, these compounds exhibit structural features resembling those of high-valent actinides, such as uranyl(VI).



Scheme 1. (a) H_3L1 = 1,3,5-tri(4'-carboxylphenyl) benzoic acid; (b) H_3L2 = 4,4',4'-nitrilotribenzoic acid.

Single crystal X-ray diffraction analysis reveals that compound **1** crystallizes in monoclinic *C*2/*c* space group, and contains a flat layer that consists of one Th(IV) ion bonding to three $L1^{3-}$ units and three terminal chloride anions (Figure 1a). Among these, three carboxylate groups from three different $L1^{3-}$ units chelate the

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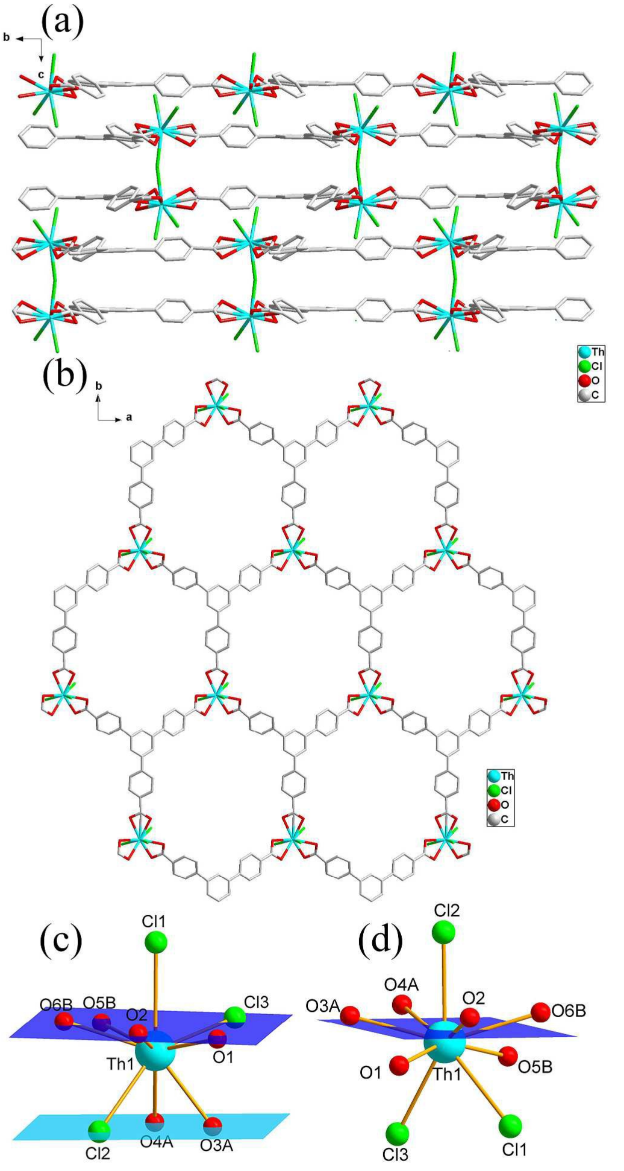

Figure 1. (a) The stacking of graphene-like layers along *a* direction for compound **1**; (b) The hexagonal (6,3)-honeycomb motif of the graphene-like layer of compound **1**; (c) The 1:5:3 coordination environment of Th(IV) in **1**; and (d) The hula-hoop coordination geometry of Th(IV) in **1**.

thorium center with Th-O distances ranging from 2.435(11) to 2.566(9) Å, comparable to the average value of 2.5 Å in other thorium organic frameworks.[9] Notably, this is the first case (the second one is compound **3** in this work) of low-valent actinide ions chelated by three carboxylate groups among the reported actinide carboxylate complexes, with other examples exhibiting coordination environment of Th(IV) chelated by double- or mono-carboxylate groups.[9b] While all the other thorium carboxylate complexes contain either monodentate[9d] or bridging (bidentate)[9h] carboxylate groups, though it is easy to form the five-member-ring chelation by nitrogen and oxygen atoms from nitrogen heterocyclic carboxylic acids.[9a, 9d] Three chloride anions are further bounded to complete the nine-coordination geometry of the local Th(IV) center with the bond distances of Th–Cl of 2.787(4), 2.775(5) and 2.856(4) Å, respectively. The overall local coordination geometry of Th(IV) ion can be best described as 9-coordinate muffin type summarized by Alvarez et al.,[10] which contains a set of three vertices related by a three-fold pseudosymmetry axis, another set of five vertices related by a colinear five-fold pseudosymmetry axis, plus the remaining vertex sitting on the axis (Figure 1c). To the best of our knowledge, compound **1** represents the first case of Th^{4+} ion adopting this coordination geometry. Note that the most prevalent coordination environment for nine-coordinate lanthanide and actinides is tricapped trigonal prism as the most isotropic one.[10]

However, this type of geometry is not able to be utilized to directly describe to overall structure of **1**. Alternatively, the coordination geometry of Th(IV) ion can be described as a distorted 9-coordinate hula-hoop with the six oxygen atoms roughly close to be in a plane with the average deviation of 0.53 Å (Figure 1d). In this case, the nine coordination sites are anisotropically occupied by six oxygen atoms from three chelating carboxylate groups, forming an equatorial plane, while three chloride anions are located from both sides of the plane. The most remarkable feature of the coordination geometry is its similarity to the hexagonal bipyramid coordination environments often observed in penta- and hexavalent actinides and the resulting dominant layered structures.[11] Similar coordination geometry is also found in a low-valent Pu(III) borate compounds $Pu_2[B_{12}O_{18}(OH)_4Br_2(H_2O)_3]\cdot 0.5H_2O$,[12a] where the resulting Pu(III) polyborate sheets that intensively resembles the sheet topologies of uranyl(VI) borate compounds.[12] Therefore, each Th(IV) ion almost shares the same equatorial plane with neighbouring Th(IV) ions and further links to six thorium centers by three $L1^{3-}$ units, affording a graphene-like layer containing open hexagonal (6,3)-honeycomb-like motifs also observed in the uranyl(VI) compound coordinated by the same ligand (Figure 1b).[8] The effective size of the nanoscale six-membered ring window is ca. 15 X 15 Å, nearly identical with the uranyl(VI) analogues.[8] π-π interactions are present between adjacent layers creating stacks along *c* axis in the structure (Figure 1a). Interestingly, the charge-balancing 1-allyl-3-methylimidazolium cations from original ionic liquid can be well-resolved in the electron density map, piercing two layers of six-membered rings vertically (Figure S1 in the ESI), deviating significantly from the common cases of templating cations present in the interlayer space. It should be noted that $[C_7H_{11}N_2]_2[Th(L1)Cl_3]$ (compound **2)** crystallizing in monoclinic space group $P2_1/c$ is also present in the products. Compound **2** adopts an identical layered structure but a different spacing between adjacent layers with compound 1, as shown in Figure S1.

Changing the rigidity and removing the conjugated feature of the ligand is achieved by replacing L1 with L2 in compound **2**, which crystallizes in trigonal $R\bar{3}c$ space group and presents a 3D metal-organic framework structure that consists of Th(IV) ions bound to six $L2^{3-}$ units and one terminal water molecule. The chelation of Th(IV) ion by three carboxylate groups of three different $L2^{3-}$ at distances of 2.660(2) and 2.501(2) Å, respectively, similar with the coordination environment in compound **1**. The remaining three L2^{3-} units coordinate the metal center with a single carboxylate oxygen atom, O3, at distance of 2.408(2) Å and an additional oxygen atom from one water molecule (O5) is further bounded to complete the overall 10-coordinate local geometry of the Th(IV) with the Th–O5 of 2.549(5) Å. Several complexes based on ten-coordinate thorium with a bicapped square antiprismatic coordination polyhedron have been reported,[9a-d, 9h] whereas the coordination feature of thorium in compound **3** represents the first example in an actinide compound containing as so called tetracapped trigonal prismatic coordination geometry (TCTPR-10) described by Alvarez et al.[14] TCTPR-10 is a unique and relatively anisotropic coordination geometry that is rarely observed even in lanthanide and transition compounds,[14-15] where the coordination of central thorium cation is formed by a polyhedron containing three parallel triangle planes built by three sets of oxygen atoms (three O3 atoms, three O1 atoms, and three O2 atoms, respectively, with the distances of 2.0 Å and 0.78 Å between the neighbouring planes), plus O5 atom in the capping position (Figure 2c), giving rise to tetracapped trigonal prism with twenty-four edges and sixteen triangle faces. Again, an alternative way to look at the coordination geometry of thorium ion in compound **3** is by combining the two upper sets of triangle planes into an averaged one as the equatorial plane (Figure 2d), similar as compound **1**, leading to overall coordination geometry of distorted 10-coordinate capped triangular cupola with ideal *C3v* symmetry,[14] which is also observed in $Pu_2[B_{12}O_{18}(OH)_4Br_2(H_2O)_3]\cdot 0.5H_2O$.[12a] As a consequence, a similar graphene-like layer based on the same (6,3) sheet topology with the effective window size of ca. 12 Å is formed in compound **3** (Figure 2b). Compared with the rigid L1^{3-} unit in compound **1**, the flexibility of N–C bonds within the L2^{3-} unit favours the connection of different Th(IV) centers between different layers through spiral triple-stranded-braids-like μ$_2$-bridges of three carboxylate groups from three different L2^{3-} units with a Th–Th distance of ca. 5.4 Å, affording a relatively dense three-dimensional framework structure of **2** (Figure 2a).

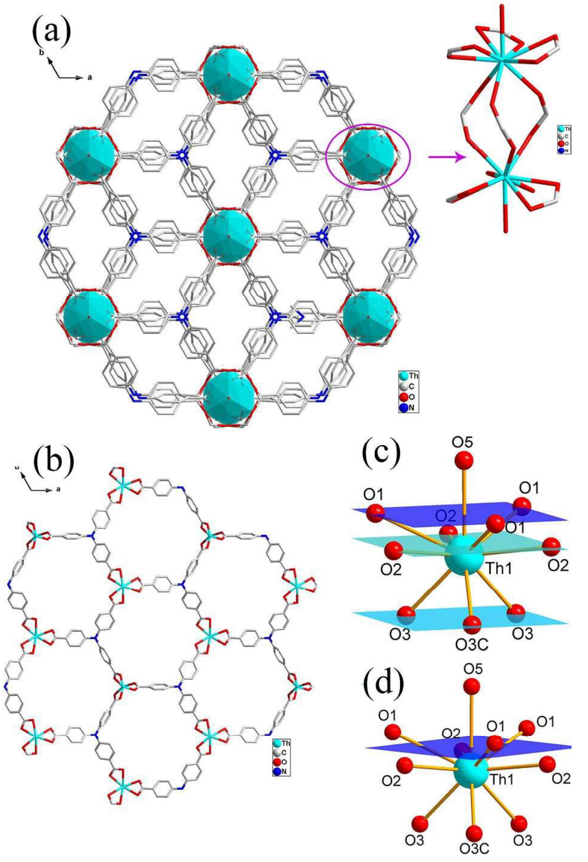

Figure 2. (a) Stacking of graphene-like layers along *b* direction for compound **3**; (b) The topology of grapheme layer in **3**; (c) the tetracapped trigonal prismatic coordination geometry of Th(IV) in compound **3**; and (d) An analogue of coordination geometry of high-valent actinide metals for compound **3**.

Compounds **1** and **2** gradually loses the crystallinity when exposed to air and quickly becomes amorphous in water indicated by powder X-ray diffraction data. This is probably due to the atypical and anisotropic geometries of the thorium(IV) center in the structure, which are not thermodynamically stable states. Whereas compound **3** can partially keep framework structure even at 400 ℃ indicated by a combination of thermalgravimetric analysis and temperature-dependent powder X-ray diffraction studies (Figure S5 and Figure S6), comparable with several robust MOF compounds based on tetravalent metal ions such as Zr^{4+}.[17] As can be seen in Figure S9, under the excitation at 420 nm, compound **3** is able to produce a bright yellow-white emission with a broad emissive feature ranging from 460 to 800 nm originated from the ligand based electronic transitions, slightly different from emission spectrum of the raw ligand. The measured internal quantum efficiency approaches 6% (Figure S11). In addition, the intensity of temperature-dependent photoluminescence of **3** decreases as the temperature rises owing to the promotion of the non-radiative emission of phonon at the elevated temperature (Figure S10).[16]

As mentioned earlier, the resemble of coordination environments of high-valent actinides for the low-valent actinides was observed in the borate system, with one of consequences that neptunium(V) and neptunium(IV) ions can co-present in the same crystal lattice site of a borate compound, confirmed by spectroscopic analysis; albeit this phenomenon cannot be resolved from the crystallographic data.[12c] This is important since low- and high-valent actinides are never expected to incorporate together owing to their crystallographically incompatible nature, evident by a series of 5f-5f heterobimetallic compounds containing separated lattice sites for both low- and high-valent actinides.[18] By adding one equivalent of UO_2^{2+} cations into the reaction system generating compounds **1** and **2**, same structure was generated with U:Th ratio of approximately 1:9 in the crystals confirmed by powder X-ray diffraction and EDS measurements (Figure S13 and Figure S14). The success doping of uranyl ions in the structure results in vibrationally coupled features in the photoluminescence spectrum characteristic for LUMO-HOMO electronic transitions of uranyl ions (Figure S15). We speculate in this case, it is highly possible that U(VI) and Th(IV) can co-crystallize in the same graphene-like layered compound by residing at the same lattice site originated from the almost identical coordination in their own compounds. However, the possibility of ion-exchange of UO_2^{2+} with the interlaminar 1-allyl-3-methylimidazolium cations cannot be ruled out at current stage.

The foregoing results demonstrate for the first time that low-valent actinide ions are able to adopt anisotropic coordination environments that resemble high-valent actinyl ions, further leading to unexpected graphene-Like layered architectures. These structure models can be used for synthesizing new type of 5f-5f heterobimetallic compounds with low- and high-valent actinides located on the same lattice site, which may find potential applications in nuclear fuel and waste management.

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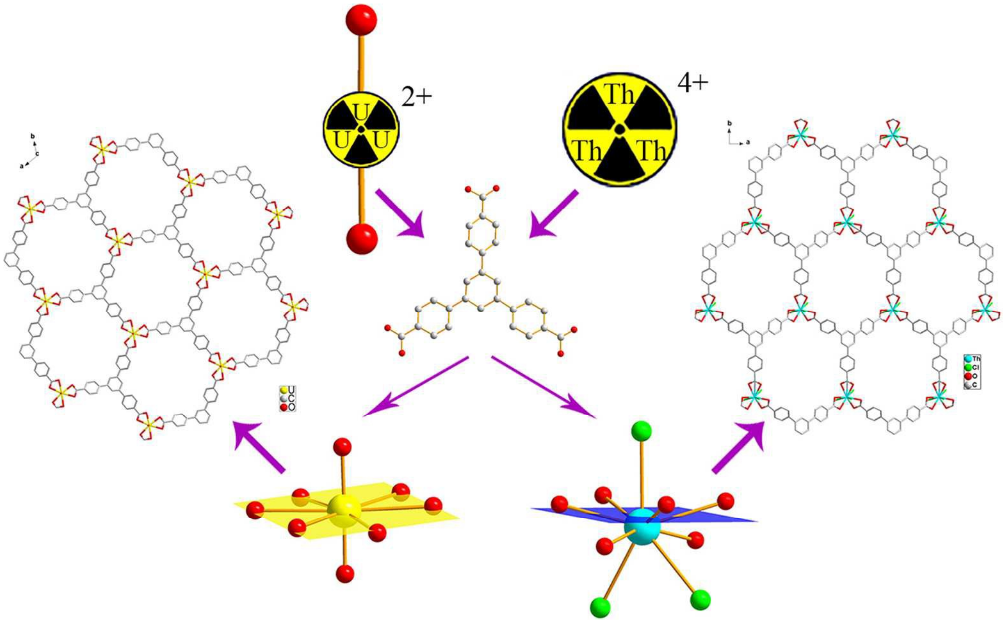

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