DOI: 10.1002/ejic.201100066

Self-Assembly of Hexanuclear Clusters of 4f and 5f Elements with Cation Specificity

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Keywords: Self-assembly / Cluster / Cerium / Thorium / Plutonium

Six hexanuclear clusters of 4f and 5f elements were synthesized by room-temperature slow concentration experiments. Cerium(IV), thorium(IV), and plutonium(IV) each form two different hexanuclear clusters, among which the cerium and plutonium clusters are isotypic, whereas the thorium clusters show more diversity. The change in ionic radii of approximately 0.08 Å between these different metal ions tunes the cavity size so that NH_4^+ (1.48 Å) has the right dimensions to assemble the cerium and plutonium clusters, whereas Cs^+ (1.69 Å) is necessary to assemble the thorium clusters. If these cations are not used in the reactions, only amorphous material is obtained.

Introduction

The self-assembly of multinuclear metal clusters with properties that can be tailored by both the identity of the metal centers and the struts between the metal centers is exemplified by homochiral tetrahedral M_4L_6 clusters, which have been shown to catalyze a number of important reactions including aza-Cope rearrangements[1–4] and allylic alcohol rearrangement[5] as well as enantioselective guest binding.[6–10] The use of square-planar metal centers (e.g. Pd^{II}) allows for the assembly of chiral hexanuclear clusters with distorted octahedral cores.[11] Larger clusters are known such as the cubooctahedral Zn^{II} cluster obtained by Kiruma and co-workers.[12]

Whereas clusters of tetravalent transition metals are well established, there are fewer reports of such assemblies with 4f or 5f elements. Rare earth elements yield higher coordination numbers and different geometries than main group elements and transition metals will allow for. Furthermore, the rare earth series offers the advantage of having exquisitely tunable ionic radii that enables sequential modifications in the properties of compounds derived from these elements. Examples of such tetravalent f element clusters include hexanuclear Ce^{IV} carboxylates that can be used as oxidants in organic synthesis[13] and mixed Ce^{IV}/Ln^{III} clusters where both metal-based and ligand-based luminescence occur;[14] 5f element clusters are far more rare. However, dodecanuclear thorium clusters with a nitride core have been described.[15] Colloidal Pu^{IV} is actually a nanoscale cluster of 38 Pu^{IV} centers with fluorite structure.[16]

In this report we describe the self-assembly of six hexanuclear anionic clusters of Ce^{IV}, Th^{IV}, and Pu^{IV} $(NH_4)_6M_6(NO_3)_{12}[C_6H_4(PO_3)(PO_3H)]_6{\cdot}9H_2O$ (M = Ce, Pu) (**Ce6-1**, **Pu6-1**), $(NH_4)_6M_6(NO_3)_{12}[C_6H_4(PO_3)(PO_3H)]_6{\cdot}3H_2O$ (M = Ce, Pu) (**Ce6-2**, **Pu6-2**), $Cs_5Th_6(H_2O)_{10}(NO_3)_6[C_6H_4(PO_3)(PO_3H)]_6{\cdot}5(NO_3){\cdot}7H_2O$ (**Th6-1**), and $Cs_8Th_6(H_2O)_4(NO_3)_{10}[C_6H_4(PO_3)(PO_3H)]_6{\cdot}4(NO_3)$ (**Th6-2**). The change in ionic radius from Ce^{IV} to Th^{IV} of approximately 0.08 Å allows for the cavity size to be tuned, and the clusters to preferentially bind cations that are best suited to the size of the cavities. Ce^{IV} and Pu^{IV} are thought to have nearly identical ionic radii, and this report expands upon our work and that of others to demonstrate similarities and differences between the chemistry of Ce^{IV} and Pu^{IV}.

Results and Discussion

The cerium and thorium clusters were synthesized by using a combinatorial approach that explored the effects of pH, counter cations (e.g. various alkali metals, alkaline earth metals, and ammonium), and stoichiometry of the reactants. The results demonstrated that the clusters form over a wide pH range (from ca. 1 to ca. 12). The clusters were crystallized by slow concentration at room temperature. For Pu^{IV}, the conditions that yielded Ce^{IV} crystals were employed. However, the starting material was Pu^{VI}, which was reduced to Pu^{IV} by using a slight excess of nitrite immediately prior to the addition of the other reagents. Crystals only form with Ce^{IV} and Pu^{IV} if NH_4^+ is present in the reaction mixture, and with Th^{IV} the crystals only form if Cs^+ is present. No other combination of common cations allowed these clusters to self-assemble and crystallize.

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201100066.

The structures of these clusters are quite complex owing to the high coordination numbers of the metal centers as shown in Figure 1. In all cases the metal centers form a distorted octahedron. For **Ce6-1** and **Pu6-1** the clusters have C_{3i} symmetry. For **Ce6-2** and **Pu6-2**, the clusters are more distorted and are in the C_i point group. Both **Th6-1** and **Th6-2** are more similar with **Ce6-2** and **Pu6-2**, and they also possess C_i symmetry. Views of the two different cluster symmetries are shown in Figure 2.

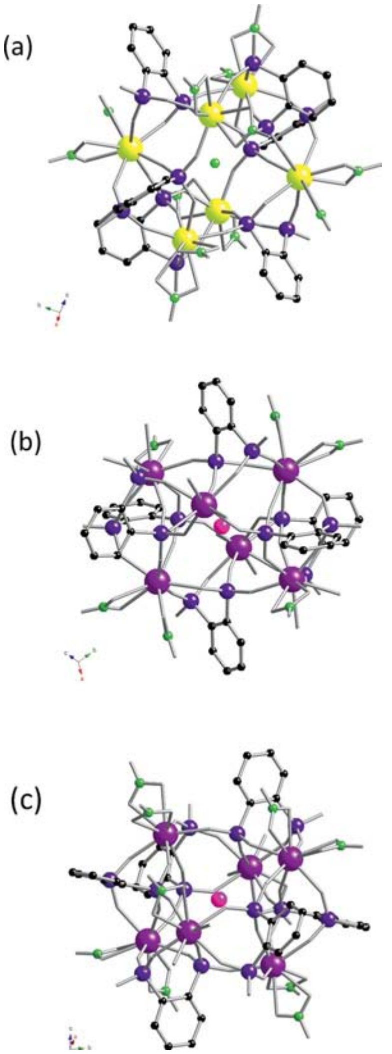

Figure 1. Views of the anionic hexanuclear Ce^{IV}, Th^{IV}, and Pu^{IV} diphosphonate clusters: $(NH_4)_6M_6(NO_3)_{12}[C_6H_4(PO_3)(PO_3H)]_6 \cdot 9H_2O$ (M = Ce, Pu) (**Ce6-1**, **Pu6-1**) and $(NH_4)_6M_6(NO_3)_{12}[C_6H_4(PO_3)(PO_3H)]_6 \cdot 3H_2O$ (M = Ce, Pu) (**Ce6-2**, **Pu6-2**) (a), $Cs_5Th_6(H_2O)_{10}(NO_3)_6[C_6H_4(PO_3)(PO_3H)]_6 \cdot 5(NO_3) \cdot 7H_2O$ (**Th6-1**) (b), $Cs_8Th_6(H_2O)_4(NO_3)_{10}[C_6H_4(PO_3)(PO_3H)]_6 \cdot 4(NO_3)$ (**Th6-2**) (c). For **Ce6-1**, **Pu6-1**, **Ce6-2**, and **Pu6-2** the guest is NH^{4+}; whereas for **Th6-1** and **Th6-2** the guest is Cs^+.

The 1,2-phenylenediphosphonate (PhP2) ligand both chelates the metal centers and bridges between them as shown in Figure 1. In all compounds, the ligand behaves in a similar manner in that one PO_3 moiety is bonded to three metal centers, whereas the other PO_3 group is bonded to only two metal centers and has one protonated O atom. The metal centers are chelated by four PO_3 groups from the two PhP2 ligands. A total of six diphosphonato ligands serve to bridge between the six metal centers, and the clusters can be generally catagorized as M_6L_6 clusters. However, this description does not take into account the high coordination numbers of the metal centers that are completed by additional chelating nitrato ligands (vide infra). The clusters are all anionic, and a single cation is trapped in the cage. Additional cations, which are needed for complete charge balance, are located between the clusters in the crystal structure.

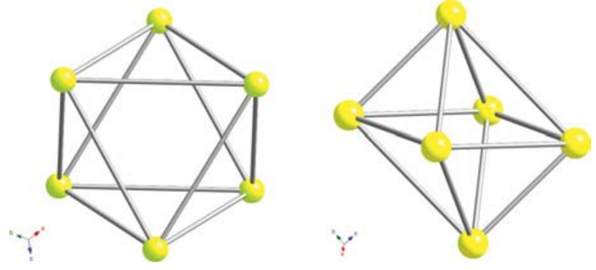

Figure 2. Views of the C_{3i} (**Ce6-1** and **Pu6-1**) and C_i (**Ce6-2**, **Pu6-2**, **Th6-1**, and **Th6-2**) symmetries of the clusters.

Ce6-1 and **Pu6-1** have the highest symmetry and in fact crystallizes in the rhombohedral space group $R\bar{3}$. There are two M^{4+} sites in the asymmetry unit, and a $\bar{3}$ operation relates these two sites to the other five sites (each site is symmetrically equivalent to five others). All six M^{4+} sites in one cluster have similar coordination environments, and are nine-coordinate with four oxygen atoms from two chelating nitrate anions and five oxygen atoms provided by five PO_3 moieties from three PhP2 units, Figure 3. The Ce–O bond lengths vary from 2.228(8) to 2.602(8) Å. The average bond length for the two cerium sites are 2.402(8) and 2.400(8) Å, respectively. Pu–O bond lengths are from 2.224(9) to 2.586(10). The average bond length for the two plutonium sites are 2.394(9) and 2.407(10), respectively.

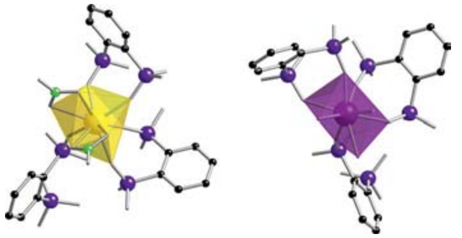

Figure 3. Views of the tricapped trigonal prism (PuO_9) and square antiprism (ThO_8) coordination environment.

Ce6-2 and **Pu6-2** are of much lower symmetry and crystallize in the triclinic space group $P\bar{1}$. Each cluster has an inversion center in the center of the cluster, and therefore there are three crystallographically unique M^{4+} ions. As a result, the six metal sites are divided into three pairs, but they still achieve similar coordination environment as found in **Ce6-1** and **Pu6-1**. The Ce–O bond lengths vary from 2.219(5) to 2.594(5) Å. The average bond length for the three cerium sites are 2.394(5), 2.396(5) and 2.395(5) Å. The

Pu–O bond lengths range from 2.226(9) to 2.612(10) Å. The average bond length for the three plutonium sites are 2.389(10), 2.391(10) and 2.392(10) Å, respectively.

The Th^{IV} cluster **Th6-1** also crystallizes in the triclinic space group $P\bar{1}$, and this cluster also has three pairs of Th sites. However, there are significant differences between the coordination of the Th^{IV} sites vs. those of the Ce^{IV} and Pu^{IV} sites. One pair of Th^{IV} ions is nine-coordinate with four oxygen atoms from two nitrate anions and five oxygen atoms donated by five PO_3 moieties from three PhP2 units. The second pair of Th^{IV} ions is also coordinated by nitrate, but there is only one nitrate anion, and the remaining two oxygen sites are occupied by water. The last pair has a lower coordination number; it is the only eight-coordinate site with no bound nitrate. The eight oxygen donors come from five different PO_3 moieties and water. The Th–O bond lengths range from 2.309(8) to 2.731(8) Å. The average bond length for the thorium sites are 2.472(8) and 2.470(8) Å for the ThO_9 tricapped trigonal prisms, and 2.430(8) Å for the ThO_8 one; Shape8 measument[17] results are D_{4d} – 5.9972, C_{2v} – 9.6577 and D_{2d} – 10.1979, showing that it is better described as a square antiprism.

The final cluster **Th6-2** is similar to **Ce6-2** and **Pu6-2**; however, they are not isostructural. All of the Th^{IV} sites are nine-coordinate, but the number of nitrate anions is different between the two Th^{IV} sites. Two pairs are chelated by two nitrate anions, whereas one pair has a single nitrate group and two water molecules. The Th–O bond lengths vary from 2.290(11) to 2.706(10) Å. The average bond length for the thorium sites are 2.464(10), 2.458(11), and 2.465(14) Å.

In general the thorium clusters show more variability in both coordination number and in the donor ligands that complete the coordination environments. It is surprising that the thorium clusters would show lower coordination numbers on average than those of Ce^{IV} or Pu^{IV} since Th^{IV} is considerably larger than these other cations. However, the longer Th–O bonds do play an important role in this cluster chemistry. The average distance between the thorium ions and the center of the clusters is 4.517(5) Å for **Th6-1** and 4.504(11) Å for **Th6-2**. In contrast, the average distances are 4.424(8) Å for **Ce6-1** and 4.405(5) Å for **Ce6-2**, and 4.420(10) for **Pu6-1** and 4.390(10) for **Pu6-2**. The change in ionic radii of approximately 0.08 Å between these different metal ions tunes the cavity size so that NH_4^+ (1.48 Å) has the right dimensions to assemble the cerium and plutonium clusters, whereas Cs^+ (1.69 Å) is necessary to assemble the thorium clusters. If these cations are not used in the reactions only amorphous material is obtained.

Conclusions

The report demonstrates the richness of 4f and 5f cluster chemistry in terms of both the highly variable coordination geometries and the ability to fine-tune the ionic radius of the metal centers. The former cannot be achieved with transition metals or main group elements, and the latter is also only achievable in the f element series. This system proved to be exquisitely sensitive to the size of the counterion, and discerning this role required a combinatorial synthetic approach.

Experimental Section

General: Confirmation of Pu^{IV} was obtained by using UV/Vis/NIR spectroscopy from single crystals, and the spectrum is provided in the Supporting Information.

Synthesis: Ce6-1 and **Ce6-2** crystals were obtained by mixing an $(NH_4)_2Ce(NO_3)_6$ solution (0.5 M,0.3 mL), 1,2-phenylenediphosphonic acid (0.5 M, 0.1 mL), NaOH(1 M, 0.1 mL) and deionized water (0.5 mL) together into a 4 mL scintillation vial; then the solvent was allowed to slowly evaporate at room temperature. Orange hexagon-plate crystals of **Ce6-1** and orange block crystals of **Ce6-2** formed. **Pu6-1** and **Pu6-2** crystals were obtained by the following procedure: A PuO_2^{2+} solution (0.37 M, 0.05 mL) and $NaNO_2$ (0.42 M, 0.05 mL) were mixed together with PhP2 (0.1 M, 0.05 mL) and NaOH (0.1 M, 0.1 mL). After 7 d, the solvent had evaporated, but no plutonium crystals had formed. The residue was mixed with NH_4NO_3 (0.05 M, 0.4 mL) and ethanol (0.4 mL). Then the upper solution was removed, and concentrated HNO_3 (0.1 mL), H_2O (0.05 mL), $NaNO_2$ (0.42 M, 0.25 mL), NH_4NO_3 (0.5 M, 0.08 mL) and PhP2 (0.1 M 0.03 mL) were added sequentially to the vial. After 6 d, some red peach crystals had formed on the bottom of the vial. The hexagon plates are **Pu6-1**, and the blocks are **Pu6-2**. **Th6-1** crystals were synthesized by mixing together a $Th(NO_3)_4$ solution (0.5 M, 0.3 mL), 1,2-phenylenediphosphonic acid (0.5 M, 0.1 mL), CsOH (1 M, 0.1 mL) in a 4 mL scintillation vial. Colourless crystals of **Th6-1** formed after slow concentration. The reaction that formed **Th6-1** crystals was adjusted by adding additional sodium phosphonoformate tribasic hexahydrate (0.5 M, 0.1 mL) and ethanol (0.5 mL). The **Th6-2** crystallized as colourless block crystals. The synthesis of 1,2-phenylenediphosphonic acid is reported in a previous study.[18]

X-ray Structural Analysis

$(NH_4)_6Ce_6(NO_3)_{12}[C_6H_4(PO_3)(PO_3H)]_6\cdot 9H_2O$ (Ce6-1): Orange hexagon plate, crystal dimensions 0.09 × 0.06 × 0.02 mm, rhombohedral, $R\bar{3}$ (No. 148), $Z = 2$, $a = 17.154(2)$ Å, $\alpha = 97.44°$, $V = 4097.7(11)$ Å^3 ($T = 100$ K), $\mu = 30.53$ cm^{-1}, $R1 = 0.0695$, $wR2 = 0.1691$. Bruker APEXII Quazar diffractometer: $\theta_{max} = 27.58°$, Mo-K_α, $\lambda = 0.71073$ Å, 0.5° ω-scans, 7513 reflections measured, 4310 independent reflections, all of which were included in the refinement.

$(NH_4)_6Ce_6(NO_3)_{12}[C_6H_4(PO_3)(PO_3H)]_6\cdot 3H_2O$ (Ce6-2): Orange block, crystal dimensions 0.08 × 0.06 × 0.04 mm, triclinic, $P\bar{1}$ (No. 2), $Z = 1$, $a = 12.811(3)$ Å, $b = 15.100(3)$ Å, $c = 15.509(4)$ Å, $\alpha = 67.957(3)°$, $\beta = 79.959(3)°$, $\gamma = 74.272(3)°$, $V = 2667.9(10)$ Å^3 ($T = 100$ K), $\mu = 28.01$ cm^{-1}, $R1 = 0.0463$, $wR2 = 0.1043$. Bruker APEXII Quazar diffractometer: $\theta_{max} = 27.57°$, Mo-K_α, $\lambda = 0.71073$ Å, 0.5° ω-scans, 12076 reflections measured, 7878 independent reflections, all of which were included in the refinement.

$(NH_4)_6Pu_6(NO_3)_{12}[C_6H_4(PO_3)(PO_3H)]_6\cdot 9H_2O$ (Pu6-1): Red-peach hexagon plate, crystal dimensions 0.05 × 0.04 × 0.02 mm, rhombohedral, $R\bar{3}$ (No. 148), $Z = 2$, $a = 17.178(3)$ Å, $\alpha = 97.541(3)°$, $V = 4924.5(13)$ Å^3 ($T = 100$ K), $\mu = 42.86$ cm^{-1}, $R1 = 0.0586$, $wR2 = 0.1386$. Bruker APEXII Quazar diffractometer: $\theta_{max} = 27.58°$, Mo-K_α, $\lambda = 0.71073$ Å, 0.5° ω-scans, 7457 reflections measured, 4023 independent reflections, all of which were included in the refinement.

$(NH_4)_6Pu_6(NO_3)_{12}[C_6H_4(PO_3)(PO_3H)]_6\cdot 3H_2O$ (Pu6-2): Red-peach block, crystal dimensions 0.06 × 0.05 × 0.02 mm, triclinic, $P\bar{1}$ (No. 2), $Z = 1$, $a = 12.756(2)$ Å, $b = 15.111(3)$ Å, $c = 15.518(4)$ Å, $\alpha = 67.966(2)°$, $\beta = 80.697(2)°$, $\gamma = 74.563(2)°$, $V = 2666.3(8)$ Å^3 ($T = 100$ K), $\mu = 39.50$ cm^{-1}, $R1 = 0.0589$, $wR2 = 0.1641$. Bruker APEXII Quazar diffractometer: $\theta_{max} = 27.50°$, Mo-K_α, $\lambda = 0.71073$ Å, 0.5° ω-scans, 12045 reflections measured, 6873 independent reflections, all of which were included in the refinement.

$Cs_5Th_6(H_2O)_{10}(NO_3)_6[C_6H_4(PO_3)(PO_3H)]_6\cdot 5(NO_3)7(H_2O)$ (Th6-1): Colourless plate, crystal dimensions 0.15 × 0.11 × 0.02 mm, triclinic, $P\bar{1}$ (No. 2), $Z = 1$, $a = 13.7663(12)$ Å, $b = 15.5589(14)$ Å, $c = 15.757(2)$ Å, $\alpha = 112.613(2)°$, $\beta = 95.377(2)°$, $\gamma = 114.9470(10)°$, $V = 2689.7(5)$ Å^3 ($T = 100$ K), $\mu = 102.16$ cm^{-1}, $R1 = 0.0430$, $wR2 = 0.1254$. Bruker APEXII Quazar diffractometer: $\theta_{max} = 27.77°$, Mo-K_α, $\lambda = 0.71073$ Å, 0.5° ω-scans, 12179 reflections measured, 9483 independent reflections, all of which were included in the refinement.

$Cs_8Th_6(H_2O)_4(NO_3)_{10}[C_6H_4(PO_3)(PO_3H)]_6\cdot 4(NO_3)$(Th6-2): Colourless plate, crystal dimensions 0.13 × 0.10 × 0.06 mm, triclinic, $P\bar{1}$ (No. 2), $Z = 1$, $a = 11.771(4)$ Å, $b = 15.553(5)$ Å, $c = 16.153(6)$ Å, $\alpha = 79.147(5)°$, $\beta = 69.623(4)°$, $\gamma = 84.013(5)°$, $V = 2720.3(16)$ Å^3 ($T = 100$ K), $\mu = 110.97$ cm^{-1}, $R1 = 0.0660$, $wR2 = 0.1624$. Bruker APEXII Quazar diffractometer: $\theta_{max} = 27.58°$, Mo-K_α, $\lambda = 0.71073$ Å, 0.5° ω-scans, 12349 reflections measured, 6632 independent reflections, all of which were included in the refinement.

Data were corrected for Lorentz-polarization effects and for absorption, structures were solved by direct methods, anisotropic refinement of F^2 by full-matrix least squares, 48 parameters.[19] Semi-empirical absorption corrections were applied by using the program SCALE (SADABS).[20] Disordered nitrate anions reside in voids in the structures of **Th6-1** and **Th6-2**. The SQUEEZE subroutine of PLATON was used to account for this electron density. Further details of the crystal structure investigation may be obtained from the Fachinformationzentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (crysdata@fiz-karlsruhe.de) on quoting numbers CSD-804046 to -804049 and -805014 to -805015.

Supporting Information (see footnote on the first page of this article): UV/Vis/NIR absorption spectrum of **Pu6-1**.

Acknowledgments

We are grateful for support provided by the U.S. Department of Energy, Heavy Elements Program, under Grant DE-SC0002215.

This material is based upon work supported as part of the Materials Science of Actinides, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0001089.

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Received: January 19, 2011