High Spin Ground States in Matryoshka Actinide Nanoclusters: A Computational Study

Han-Shi Hu and Nikolas Kaltsoyannis*

Abstract: Inspired by the experimentally synthesized Na$_{12}$@[UO$_2$]$_3$(O$_2$)$_3$S$_{39}$6 ("Na$_{12}$@U$_{20}$") cluster, we have explored computationally the substitution of the Na cations by other metals. 6 other M$_{12}$@U$_{20}$ systems are found to be stable (M = K, Rb, Cs, Ag, Mg, Fe$^{2+}$). For 3 of these (Mg$^{2+}$, Ag$^+$ and Na$^+$), the cluster can support a group 16 diamon at its centre, forming a new type of Matryoshka ("Russian Doll") actinide nanocluster E@M$_{12}$@U$_{20}$ (E = S$^2$, Se$^2$, Te$^2$ and Po$^2$). These systems have 3-shell, onion-like geometries with nearly perfect $I_h$ symmetry. Seeking to create clusters with very high-sing ground states, we have replaced M by Mn$^{2+}$ and U$_{20}$ by Np$_{20}$ and Pu$_{20}$, generating clusters with maximum possible $S$ values of $80/2$ and $100/2$ respectively. Only in the presence of a central S$^2$, however, are these electronic configurations the most stable; the novel Matryoshka Pu nanocluster S@Mn$_{12}$@Pu$_{20}$ is predicted to have the highest ground state spin yet reported for a molecular cluster.

The search for molecules with very high spin ground states remains an active area of research, in part motivated by the burgeoning field of single molecule magnetism and its potential application in information storage, spintronics and quantum computing. 1, 2 Many high-spin molecules have been reported following the discovery of the S = 20/2 Mn$_{12}$ single-molecule magnet in 1993.3 Two years later, an Fe$_{19}$ molecular cluster with S = 33/2 was discovered, and held the spin record 4 until 2000, when two heteronuclear clusters Mn$_6$M$_6$ (M = Mo and W) with S = 39/2 were characterized.5 Four years later the bar was further raised when an Mn$_{25}$ cluster with S = 51/2 was reported.6 Since then, S = 83/2 has been established (by mixing high-spin Mn(II) and Mn(III) in large clusters),7 and the largest S value for a molecular cluster known to date is 90/2, from an Fe$_{46}$ giant-spin nanocluster.8 In this contribution, we use computational quantum chemistry to explore the geometric and electronic structures of actinide nanoclusters. We report the first multi-shell, Matryoshka ("Russian Doll") actinide-transition metal complexes and, by judicious choice of 5f and 3d elements, establish a new record high-spin ground state for a molecular cluster.

The linear uranyl ion UO$_2^{2+}$ is ubiquitous in uranium chemistry and, over the last few years, a wide range of self-assembled uranyl peroxide nanoclusters has been synthesized, including more than forty with closed cages constructed from up to 60 uranyl building blocks. 9,10,11 These have highly symmetric fullerene topologies, and can encapsulate s block cations, raising intriguing possibilities for the design of actinide materials at the nanocluster scale.12 Outside of the laboratory, these uranyl-based nanoclusters are potentially of environmental significance, as they could enhance the corrosion of spent nuclear fuel, play a role in the migration of uranium in the natural environment, and be key intermediates in the formation of uranyl containing minerals from aqueous uranyl compounds. 13, 14 Of these nanoclusters, Na$_{12}$@[UO$_2$]$_3$(O$_2$)$_3$S$_{39}$6-9 denoted Na$_{12}$@U$_{20}$ herein, is the smallest fullerene cluster; it contains twelve pentagons, each built from five UO$_2^{2+}$ and five O$_2$-$^-$ ligands, and has near $I_h$ symmetry. It can be considered to consist of two shells, an outer [(UO$_2$)$_{20}$(O$_2$)$_{36}$]$^{20^-}$ shell (U$_{20}$ for short) and an inner Na$_{12}^{12+}$ shell (Na$_{12}$) encapsulated inside U$_{20}$, as shown in Figure 1. Each uranyl ion is coordinated by three O$_2$-$^-$ ligands, and each peroxide ligand is shared by two uranyl ions. Herein, we use density functional theory (DFT) to design and explore novel nanoclusters based on Na$_{12}$@U$_{20}$ via modifications of both the inner and outer shells. Details of our computational methodology are given in the Supporting Information.

Figure 1. Ball and stick representation of [Na$_{12}$@U$_{20}$]$^{3-}$ and its breakdown into outer shell U$_{20}$ and inner shell Na$_{12}^{12+}$ fragments. Uranium atoms in blue, oxygen atoms in red and sodium atoms in purple.

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Supporting information for this article is given via a link at the end of the document.
By contrast, the substantially radical bonding characteristics. Densities of just over 0.2, suggestive of incipient result in appreciably lengthened U=O.

Regular uranyl monocationic M\(^{2+}\) essentially linear parameters are as structures were obtained well as.

Due to interactions O bond length of one another U and Mg\(^{2+}\), Na\(^{+}\), K\(^{+}\), Rb\(^{+}\) and Cs\(^{+}\).

Table 1. Selected angles (°) and bond lengths (Å) from the DFT-optimized (PBE/TZP) structures of M\(_{12}\)@U\(_{20}\) (M = Fe\(^{2+}\), Mg\(^{2+}\), Ag\(^{+}\), Na\(^{+}\), K\(^{+}\), Rb\(^{+}\) and Cs\(^{+}\)).

<table>
<thead>
<tr>
<th>M</th>
<th>E = S</th>
<th>E = Se</th>
<th>E = Te</th>
<th>E = Po</th>
</tr>
</thead>
<tbody>
<tr>
<td>U-O-O-U</td>
<td>142.56</td>
<td>142.82</td>
<td>143.70</td>
<td>143.45</td>
</tr>
<tr>
<td>U=O</td>
<td>2.09</td>
<td>2.09</td>
<td>2.09</td>
<td>2.08</td>
</tr>
<tr>
<td>O-O(peroxo)</td>
<td>1.47</td>
<td>1.47</td>
<td>1.47</td>
<td>1.47</td>
</tr>
<tr>
<td>U-O@M</td>
<td>2.26</td>
<td>2.27</td>
<td>2.27</td>
<td>2.29</td>
</tr>
<tr>
<td>E-M</td>
<td>3.17</td>
<td>3.18</td>
<td>3.22</td>
<td>3.24</td>
</tr>
<tr>
<td>E-Cu</td>
<td>3.72</td>
<td>3.73</td>
<td>3.73</td>
<td>3.75</td>
</tr>
<tr>
<td>U=O</td>
<td>6.34</td>
<td>6.37</td>
<td>6.45</td>
<td>6.48</td>
</tr>
<tr>
<td>U-O@M</td>
<td>11.59</td>
<td>11.60</td>
<td>11.61</td>
<td>11.65</td>
</tr>
</tbody>
</table>

Table 2. Selected angles (°) and bond lengths (Å) from the DFT-optimized (PBE/TZP) structures of E@M\(_{12}\)@U\(_{20}\) (M = Mg\(^{2+}\), Ag\(^{+}\) and Na\(^{+}\); E = S, Se and Te and Po).

<table>
<thead>
<tr>
<th>M</th>
<th>E = S</th>
<th>E = Se</th>
<th>E = Te</th>
<th>E = Po</th>
</tr>
</thead>
<tbody>
<tr>
<td>U-O-O-U</td>
<td>141.39</td>
<td>141.84</td>
<td>141.84</td>
<td>142.78</td>
</tr>
<tr>
<td>O-O(peroxo)</td>
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<td>1.88</td>
<td>1.88</td>
<td>1.88</td>
</tr>
<tr>
<td>O-M</td>
<td>2.39</td>
<td>2.39</td>
<td>2.39</td>
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<tr>
<td>E-M</td>
<td>3.99</td>
<td>3.03</td>
<td>3.03</td>
<td>3.14</td>
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<td>E-Cu</td>
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<td>4.17</td>
<td>4.14</td>
<td>4.21</td>
</tr>
<tr>
<td>U=O</td>
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<td>6.06</td>
<td>6.13</td>
<td>6.27</td>
</tr>
<tr>
<td>U-O@M</td>
<td>12.04</td>
<td>12.10</td>
<td>12.10</td>
<td>12.05</td>
</tr>
</tbody>
</table>

Table 1 collects key structural data for Na\(_{12}\)@U\(_{20}\). The peroxide O-O bond length of c. 1.47 Å is significantly shorter in the U\(_{20}\) cage than in the naked anion (c. 1.68 Å), due to transfer of anti-bonding electrons from O\(_{2}^{-}\) to the vacant orbitals of UO\(_{2}^{-}\). The significantly bent dihedral angle \(\angle U-O-O-U\) plays an important role in forming the ball-like U\(_{20}\) cage.\(^{15}\) Due to interactions with the inner Na\(_{12}\) shell, the inward U=O bond length (U=O\(_{in}\)) is longer than the outward one (O\(_{out}=U\), 1.87 vs 1.84 Å).

With Na\(_{12}\)@U\(_{20}\) in hand, we searched for other cation shells that can be stabilized inside the U\(_{20}\) cage. We scanned all the alkali, alkaline-earth and divalent 3d-metal cations, as well as Ag\(^{+}\) as its radius is close to that of Na\(^{+}\). True minimum structures were obtained for Mn\(_{12}\)@U\(_{20}\) with M = K\(^{+}\), Rb\(^{+}\), Cs\(^{+}\), Ag\(^{+}\), Mg\(^{2+}\) and Fe\(^{2+}\). These new ncloclusters retain the same near \(i_{h}\) topology of the Na\(_{12}\) system; the optimized geometric parameters are collected in Table 1. Varying the cation does not affect the \(\angle U-O-O-U\) dihedral angles very much - all are within 2.5° of one another. The uranyl units are all essentially linear, and the U-O distances in the systems with monocationic M\(_{12}\) cages are little perturbed from those of regular uranyl\(^{VI}\) complexes. By contrast, the substantially stronger electrostatics of the Fe\(^{2+}\) and Mg\(^{2+}\)-based M\(_{12}\) cages result in appreciably lengthened U=O\(_{in}\). Interestingly, the formally closed-shell O\(_{in}\) atoms in these systems have spin densities of just over 0.2, suggestive of incipient two-centre radical bonding characteristics.

The Fe\(_{12}\) cage has the smallest “diameter” (5.67 Å, taken as the farthest distance between Fe\(^{2+}\) ions) consistent with it having the smallest cation radius and highest positive charge. By contrast, the Cs\(_{12}\) cage has the largest diameter (9.51 Å), due to Cs\(^{+}\) being the largest monovalent ion considered. The diameter of the outer shell U\(_{20}\) cage (taken as the largest U-O distance) varies relatively little as a function of the inner M\(_{12}\) cage, ranging from 11.63 to 12.68 Å between M = Fe\(^{2+}\) and M = Cs\(^{+}\). The O\(_{out}=U\) distances, the largest distances between inward-pointing uranyl oxygens, have a larger range, 7.34 to 9.02 Å. Figure 2 collects these diameter data; the inner M\(_{12}\) shell changes much the most of the three datasets, showing the versatility of the U\(_{20}\) cage for the encapsulation of cation shells.

All of the above Mn\(_{12}\)@U\(_{20}\) clusters have closed-shell electronic structures except Fe\(_{12}\)@U\(_{20}\). This arises from the four unpaired 3d electrons on each Fe\(^{2+}\) centre. These are coupled ferromagnetically in our calculations, giving a system with S = 48/2. We tried to increase this still further by encapsulating a cage of 12 Mn\(^{2+}\) ions (each of which has five unpaired 3d electrons) but it did not prove possible to locate a true minimum structure for Mn\(_{12}\)@U\(_{20}\).

![Figure 2](image-url)
Matryoshka ("Russian Doll") nanoclusters have icosahedral structures and general formula E@M_{12}@E_{20} (Figure 3) where E is a main group element and M is a metal atom.\textsuperscript{16, 17, 18, 19} We were interested to see if we could generate analogues of such systems using our M_{12}@U_{20} clusters, thereby forming the first actinide Matryoshka clusters, in which uranyl ions replace main group atoms as the basic building block of the outer shell. We therefore placed a group 16 dianion, O\textsuperscript{2−}, S\textsuperscript{2−}, Se\textsuperscript{2−}, or Po\textsuperscript{2−} into the centre of each of our seven M_{12}@U_{20} clusters. Of these, only Mg_{12}@U_{20}, Ag_{12}@U_{20}, and Na_{12}@U_{20} yielded optimized true minimum structures, and then only with the heavier group 16 anions; O\textsuperscript{2−} did not stay in the centre of the cluster, but migrated to sit over one of the M\textsubscript{12} cages. It therefore appears that the stability of the E@M\textsubscript{12}@U\textsubscript{20} motif is limited to the heavier group 16 dianions in conjunction with M\textsubscript{12} cages with a rather narrow range of diameters; Mg\textsuperscript{2+}, Ag\textsuperscript{+}, and Na\textsuperscript{+} yield cages with diameters from 6.77 to 7.84 Å. Key structural data for our new actinide Matryoshka nanoclusters are collected in Table 2, and a summary of all of our U\textsubscript{20}-based systems is given in Scheme 1. Table 2 shows that changing the central E\textsuperscript{2−} has only a minor effect on the size of the M\textsubscript{12} and U\textsubscript{20} cages.

Table 3. Relative energies (kJ/mol) of the four highest spin electronic configurations of Mn\textsubscript{12}@An\textsubscript{20} and S@Mn\textsubscript{12}@An\textsubscript{20} (An=NP, Pu), computed with three different functional/basis set combinations.

\[
\begin{array}{l|ccc|ccc}
\hline
 & \text{VWN/DZ} & \text{PBE/TZP} & \text{PBE/TZ2P} \\
\hline
\text{S@Mn}_{12}@\text{NP}_{20}^a & 59.54 & 63.97 & 86.15 \\
S = 80/2 & 0.00 & 82.59 & 57.32 \\
S = 78/2 & 13.56 & 0.00 & 0.00 \\
S = 76/2 & 38.58 & 39.66 & 44.60 \\
S = 74/2 & 56.27 & 36.15 & 61.67 \\
\hline
\text{Mn}_{12}@\text{NP}_{20} & 0.00 & 0.00 & 0.00 \\
S = 100/2 & 45.44 & 36.15 & 23.72 \\
S = 98/2 & 115.52 & 73.72 & 47.32 \\
S = 96/2 & 148.62 & 97.40 & 95.77 \\
S = 94/2 & 182.72 & 166.73 & 131.13 \\
\hline
\end{array}
\]
The electronic occupation is Aufbau for $S = 80/2$ and $78/2$, and non-Aufbau for $S = 76/2$ and $74/2$, with occupied $\beta$ spin orbitals energetically higher than unoccupied $\alpha$ spin orbitals. The electronic occupation is Aufbau for $S = 100/2$, and non-Aufbau for $S = 98/2, 96/2$ and $94/2$ with occupied $\beta$ spin orbitals energetically higher than unoccupied $\alpha$ spin orbitals.

In summary, systematic DFT investigation has revealed that seven cation cages are stable within an outer $U_{20}$ shell, forming $M_{12}@U_{20}$ nanoclusters ($M = \text{Fe}^{2+}, \text{Mg}^{2+}, \text{Ag}^+, \text{Na}^+, \text{K}^+, \text{Rb}^+$ and $\text{Cs}^+$). Three of these systems ($M = \text{Na}^+, \text{Mg}^{2+}$ and $\text{Ag}^+$) can stabilise a chalcogen dianion at their centre, forming novel Matryoshka actinide nanoclusters $E@M_{12}@U_{20}$ ($M = \text{Na}$ and $\text{Mg}$; $E = \text{S}, \text{Se}, \text{Te}$ and $\text{Po}$). Replacement of $M$ with $\text{Mn}^{2+}$ and $U_{20}$ with $\text{Np}_{20}$ and $\text{Pu}_{20}$ yields stable nanoclusters with very high spin ground states; $S@\text{Mn}_{12}@\text{Pu}_{20}$ has the highest $S$ value yet reported for a molecular cluster, 100/2. The presence of the central $S^2$ is essential for stabilising the highest spin electronic configurations. Work is underway to establish the origin of the stability afforded by the group 16 dianion. In the meantime, we hope that our calculations will stimulate experimental search for Matryoshka actinide nanoclusters.

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Keywords: Actinyl • Matryoshka nanocluster • DFT • High-spin state • peroxide
COMMUNICATION

Novel actinide nanoclusters with Matryoshka ("Russian Doll") geometries have new record high-spin ground states.

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