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

Han-Shi Hu and Nikolas Kaltsoyannis*

Abstract: Inspired by the experimentally synthesized $\text{Na}_{12}@[(\text{UO}_2)(\text{O}_2)_{1.5}]_{20}^{8-}$ ("Na₁₂@U₂₀") cluster, we have explored computationally the substitution of the Na cations by many other metals. 6 other $\text{M}_{12}@U_{20}$ systems are found to be stable ($\text{M} = \text{K}^+, \text{Rb}^+, \text{Cs}^+, \text{Ag}^+, \text{Mg}^{2+}, \text{Fe}^{2+}$). For 3 of these ($\text{Mg}^{2+}, \text{Ag}^+$ and Na^+), the cluster can support a group 16 dianion at its centre, forming a new type of Matryoshka ("Russian Doll") actinide nanocluster $\text{E}@M_{12}@U_{20}$ ($\text{E} = \text{S}^{2-}, \text{Se}^{2-}, \text{Te}^{2-}$ and Po^{2-}). These systems have 3-shell, onion-like geometries with nearly perfect I_h symmetry. Seeking to create clusters with very high-spin 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 $\text{S}@Mn_{12}@Pu_{20}$ 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 record⁴ until 2000, when two heteronuclear clusters Mn_9M_6 ($\text{M} = \text{Mo}$ 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_{45} 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 OUO_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, $\text{Na}_{12}@[(\text{UO}_2)(\text{O}_2)_{1.5}]_{20}^{8-}$,⁹ denoted $\text{Na}_{12}@U_{20}$ herein, is the smallest fullerene cluster; it contains twelve pentagons, each built from five UO_2^{2+} and five O_2^{2-} ligands, and has near I_h symmetry. It can be considered to consist of two shells, an outer $[(\text{UO}_2^{2+})_{20}(\text{O}_2^{2-})_{30}]^{20-}$ 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^{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 $\text{Na}_{12}@U_{20}$ 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 $[\text{Na}_{12}@U_{20}]^{8-}$ and its breakdown into outer shell U_{20}^{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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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^+).

	$M = Fe^{2+}$	$M = Mg^{2+}$	$M = Ag^+$	$M = Na^+$	$M = K^+$	$M = Rb^+$	$M = Cs^+$
$\angle U-O-O-U$	142.75	145.01	141.45	143.75	146.58	147.13	147.61
$\angle O=U=O$	179.95	179.97	179.97	179.98	179.88	179.89	179.92
$O_{out}=U$	1.79	1.78	1.84	1.84	1.84	1.83	1.83
$U=O_{in}$	2.16	2.11	1.90	1.87	1.85	1.84	1.83
O-O (peroxo)	1.47	1.47	1.47	1.47	1.47	1.47	1.46
$U-O_{peroxo}$	2.30	2.31	2.38	2.38	2.42	2.43	2.47
$M-M_{nearest}$	3.01	3.56	3.72	4.12	4.56	4.73	4.99
$O_{in}-M$	2.18	2.30	2.51	2.60	2.78	2.85	2.98

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^+ ; $E = S, Se, Te$ and Po).

	$M = Mg^{2+}$				$M = Ag^+$				$M = Na^+$			
	$E = S$	$E = Se$	$E = Te$	$E = Po$	$E = S$	$E = Se$	$E = Te$	$E = Po$	$E = S$	$E = Se$	$E = Te$	$E = Po$
$\angle U-O-O-U$	142.56	142.82	143.70	143.45	141.39	141.84	141.84	142.78	141.33	142.17	142.51	142.70
$\angle O=U=O$	179.99	179.99	179.95	179.87	179.91	179.84	179.84	179.88	179.98	179.97	179.94	179.99
$O_{out}=U$	1.79	1.79	1.79	1.79	1.85	1.85	1.85	1.85	1.85	1.85	1.85	1.85
$U=O_{in}$	2.09	2.09	2.09	2.08	1.88	1.88	1.88	1.88	1.87	1.87	1.86	1.86
O-O (peroxo)	1.47	1.47	1.47	1.47	1.47	1.47	1.47	1.47	1.47	1.47	1.47	1.47
$U-O_{peroxo}$	2.31	2.31	2.31	2.31	2.39	2.39	2.39	2.39	2.39	2.39	2.39	2.39
$M-M_{nearest}$	3.33	3.36	3.40	3.41	3.16	3.21	3.18	3.28	3.48	3.50	3.61	3.64
$O_{in}-M$	2.26	2.27	2.27	2.29	2.53	2.54	2.53	2.54	2.53	2.52	2.55	2.54
E-M	3.17	3.18	3.22	3.24	2.99	3.03	3.03	3.14	3.33	3.34	3.45	3.45
E- O_{in}	3.72	3.73	3.73	3.75	4.16	4.17	4.14	4.21	4.16	4.16	4.18	4.19
$M-M_{max}$	6.34	6.37	6.45	6.48	5.98	6.06	6.13	6.27	6.66	6.69	6.80	6.92
$U-U_{max}$	11.59	11.60	11.61	11.65	12.04	12.10	12.10	12.05	12.05	12.06	12.08	12.10

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^{2-} to the vacant orbitals of UO_2^{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 $M_{12}@U_{20}$ with $M = K^+, Rb^+, Cs^+, Ag^+, Mg^{2+}$ and Fe^{2+} . These new nanoclusters retain the same near I_h topology of the Na 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 2.50° 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-U 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 $O_{in}-O_{in}$ 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 $M_{12}@U_{20}$ 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. X-X diameters ($X = U, O_{in}, M$) of $M_{12}@U_{20}$ based on DFT optimization.

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.^{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^{2-} , S^{2-} , Se^{2-} , Te^{2-} or Po^{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^{2-} did not stay in the centre of the cluster, but migrated to sit over one of the M_3 triangles of the M_{12} cages. It therefore appears that the stability of the $E@M_{12}@U_{20}$ motif is limited to the heavier group 16 dianions in conjunction with M_{12} cages with a rather narrow range of diameters; Mg^{2+} , Ag^+ and Na^+ 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_{20} -based systems is given in Scheme 1. Table 2 shows that changing the central E^{2-} has only a minor effect on the size of the M_{12} and U_{20} cages.

Figure 3. Schematic representation of a Matryoshka cluster with a three-layer Russian doll structure and general formula $E@M_{12}@E_{20}$ (E is a main-group element and M is a metal atom). The red in the centre represents E, the blue cage represents the inner M_{12} shell and the outer grey cage represents the E_{20} .

The uranyl ion contains U(VI) and hence has no unpaired electrons. Replacing uranyl by its heavier congenors

neptunyl^{VI} (NpO_2^{2+}) or plutonyl^{VI} (PuO_2^{2+}) will introduce, respectively, one and two unpaired 5f electrons per actinyl unit to the nanoclusters. In searching for systems with very high-spin ground states, we tried encapsulating cages of twelve Mn^{2+} ions in Np_{20} and Pu_{20} cages. Pleasingly, although Mn_{12} is not stable in U_{20} (*vide supra*), it is so inside the heavier actinyl cages. Table 3 collects the relative energies of the highest spin states of $Mn_{12}@Np_{20}$ and $Mn_{12}@Pu_{20}$, computed at various levels of DFT and basis set. Unfortunately, the highest possible spin state ($S = 80/2$ for the Np_{20} cluster ($S = 60/2$ from the 12 $3d^5$ Mn^{2+} ions + $S = 20/2$ from the 20 $5f^1$ NpO_2^{2+} ions) and 100/2 for Pu_{20} (as for the Np_{20} system but with two 5f electrons per actinyl)) is not the most stable, with lower spin, non-Aufbau configurations being much more energetically preferred. Undeterred, we moved on to consider neptunyl and plutonyl analogues of our new Matryoshka nanoclusters. The only group 16 dianion which is stable in both $E@Mn_{12}@Np_{20}$ and $E@Mn_{12}@Pu_{20}$ is S^{2-} . The heavier chalcogen ions are stable in the neptunium system but not in Pu_{20} . Remarkably, the presence of the closed-shell S^{2-} at the centre of the clusters significantly modifies the energetic ordering of the highest spin states, as shown in Table 3. Specifically, for both $S@Mn_{12}@Np_{20}$ and $S@Mn_{12}@Pu_{20}$ at all three levels of theory employed, the fully Aufbau, highest spin configuration is comfortably the most stable, by 23.72 and 24.64 kJ/mol respectively for the neptunium and plutonium systems at the highest level of theory employed (PBE/TZ2P). We are therefore pleased to introduce $S@Mn_{12}@Pu_{20}$ as the new record holder for maximum ground state S in a molecular cluster.

Scheme 1. The $M_{12}@U_{20}$ and $E@M_{12}@U_{20}$ nanoclusters reported in this work.

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

	$Mn_{12}@Np_{20}$			$S@Mn_{12}@Np_{20}^a$		
	VWN/DZ	PBE/TZP	PBE/TZ2P	VWN/DZ	PBE/TZP	PBE/TZ2P
$S = 80/2$	59.54	63.97	86.15	0.00	0.00	0.00
$S = 78/2$	0.00	82.59	57.32	45.44	36.15	23.72
$S = 76/2$	13.56	0.00	0.00	115.52	73.72	47.32
$S = 74/2$	38.58	38.66	44.60	148.62	97.40	95.77
	$Mn_{12}@Pu_{20}$			$S@Mn_{12}@Pu_{20}^b$		
	VWN/DZ	PBE/TZP	PBE/TZ2P	VWN/DZ	PBE/TZP	PBE/TZ2P
$S = 100/2$	56.27	36.15	61.67	0.00	0.00	0.00
$S = 98/2$	0.00	32.59	48.28	43.89	45.52	24.64
$S = 96/2$	/	0.00	0.00	115.10	108.87	78.91
$S = 94/2$	40.04	58.99	52.72	182.72	166.73	131.13

^a The electronic occupation is Aufbau for $S = 80/2$ and $78/2$, and non-Aufbau for $S = 76/2$ and $74/2$, with occupied β spin orbitals energetically higher than unoccupied α spin orbitals.

^b The electronic occupation is Aufbau for $S = 100/2$, and non-Aufbau for $S = 98/2$, $96/2$ and $94/2$ with occupied β spin orbitals energetically higher than unoccupied α 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 ($M = Fe^{2+}$, Mg^{2+} , Ag^+ , Na^+ , K^+ , Rb^+ and Cs^+). Three of these systems ($M = Na^+$, Mg^{2+} and Ag^+) can stabilise a chalcogen dianion at their centre, forming novel Matryoshka actinide nanoclusters $E@M_{12}@U_{20}$ ($M = Na$ and Mg ; $E = S$, Se , Te and Po). Replacement of M with Mn^{2+} and U_{20} with Np_{20} and Pu_{20} yields stable nanoclusters with very high spin ground states; $S@Mn_{12}@Pu_{20}$ 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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