A Journey inside the U$_{28}$ Nanocapsule


Introduction

A better understanding of actinide chemistry is the foundation for developing safe and efficient nuclear fuel cycle technology, including fuel reprocessing, waste treatment, and environmental remediation. The recent discovery of discrete, aqueous-phase, actinide polynuclear clusters of Th, U, Np, and Pu[1–3] are inspiring the development of new techniques for actinide separation towards understanding contaminant speciation and transport in the environment. The most versatile of these actinide clusters are the uranyl–peroxides pioneered by Burns and co-workers;[1,2] however, we still have much to learn about the mechanisms that drive their self-assembly. Computational studies have shown[4,5] that alkali metal cations strongly affect cluster topology by templating and stabilizing square-, pentagonal-, and hexagonal macrocycle building blocks, which then condense to form nanocapsules. One of the most-developed members of this family is U$_{28}$, which was first synthesized by Burns et al. as $[\text{K}_{16^{-}}(\text{H}_{2}\text{O})_{2}[\text{UO}_{2}(\text{O}_{2})_{2}(\text{H}_{2}\text{O})_{2}]_{4}(\text{UO}_{2}\text{O}_{2})_{1.5}]^{14}$ (U@K$_{16}$U$_{28}$).[2] The uranyl shell in U@K$_{16}$U$_{28}$ is made up of four hexagonal faces and twelve fused pentagonal rings, and it conceptually matches the tetrahedral (T$_d$) isomer of fullerene C$_{28}$ (Figure 1). Inside the U$_{28}$ capsule, the hexagonal and pentagonal faces host M$'$ and M$''$ alkali cations, respectively, which bond to the inner, terminal O (the so-called “yl”) oxygen atoms. At the center of the U$_{28}$ cluster is an encapsulated anion (a uranyl anion in the case of U@K$_{16}$U$_{28}$). Nyman et al.[9] expanded the U$_{28}$ family by using mixtures of cations and either [UO$_2$(O$_2$)$_3$]$^{4-}$ or M(O$_2$)$_4$$^{3-}$ as the central anion to produce U@M$'$$_{12}$M$''$$_{12}$U$_{28}$ and M@M$'$$_{12}$M$''$$_{12}$U$_{28}$, with M = Ta, Nb; M$'$ = Rb, Cs; and M$''$ = K. The location of Rb$^+$ and Cs$^+$ at the hexagonal M$'$ sites and K$^+$ at the pentagonal M$''$ sites reflected the distinct selectivity of the cations for the uranyl macrocycles, which agreed with our recently reported calculations.[5] These calculations also predicted that Na$^+$ cations would occupy the M$''$ sites, and, indeed, new structures presented herein (Ta@Cs$_{12}$Na$_{12}$U$_{28}$ and Nb@Rb$_{12}$Na$_{12}$U$_{28}$) are likewise in agreement. However, structural uncertainties still remained in the central anion. Neither [UO$_2$(O$_2$)$_3$]$^{4-}$ nor...
M(O_2)^{4-} could be fully described from X-ray data owing to disorder; however, these species, which fully occupied the central cavity, provided an appropriate charge balance. Obtaining a clear snapshot of the bonding between the central anion template and the alkali templates would provide valuable insight into the self-assembly process from rings into capsules, as well as the aqueous behavior of these capsules. With an ample series of structures that systematically varied in terms of the alkali cations and central anions in hand, we had a unique opportunity to correlate theory and experiment towards understanding the stabilization effects in these cluster templates. Herein, we report density functional theory (DFT) calculations and experimental data (X-ray structures and electrochemical response) on full uranyl nanocapsules, in which remarkable agreement between experiment and theory was achieved.

Results and Discussion

**Structural parameters and relative stability:** Tetraperoxide [M(O_2)_4]^{3-} (M = Ta, Nb) species are not perfectly tetrahedral but rather have D_{3d} symmetry.[7] Because the uranyl nanocapsule framework ideally has T_d symmetry, only two distinct symmetric orientations of the D_{3d} object inside the nanocapsule were possible: one that retained D_{3d} symmetry and one with C_{3v} symmetry (Figure 2). In the D_{3d} isomer, the peroxido ligands of M(O_2)_4 were oriented in such a way that each ligand pointed towards one face of the tetrahedron that was formed by the M' hexagonal sites; in other words, towards one of the four triangles that were formed by three M' sites. In the C_{3v} isomer, the M(O_2)_4 pseudo-tetrahedron was oriented in the opposite manner, so each peroxo ligand pointed towards the vertices of the tetrahedron that was formed by the M' hexagonal sites. Thus, the geometries of [M@M',M_{3d}(UO_2(O_2))_{12}]^{2+} (M = Ta, Nb; M' = K, Rb, Cs; M' = Na, K) were fully optimized under the constraints of both the D_{3d} or C_{3v} point-symmetry groups.

The experimental X-ray[8] geometrical parameters of the inner tetraperoxide unit. provided an appropriate charge balance.

Table 1. Selected bond lengths [Å] and angles [°] for the computed D_{3d} structure and X-ray parameters[9] of M(O_2)_4|M';Na;U_{28} (M = Nb, M' = Rb; M = Ta, M' = Cs).[9]

<table>
<thead>
<tr>
<th>M = Nb</th>
<th>M = Ta</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>M = Nb</strong></td>
<td><strong>M = Ta</strong></td>
</tr>
<tr>
<td>U=O_{u,}\text{out}</td>
<td>1.85</td>
</tr>
<tr>
<td>U=O_{v,}\text{out}</td>
<td>1.87–1.88</td>
</tr>
<tr>
<td>U=O_{u,}\text{in}</td>
<td>2.37–2.38</td>
</tr>
<tr>
<td>U=O_{v,}\text{in}</td>
<td>2.34–2.36</td>
</tr>
<tr>
<td>O–O</td>
<td>1.48</td>
</tr>
<tr>
<td>M=O_{u,}\text{out}</td>
<td>3.18–3.26</td>
</tr>
<tr>
<td>Na=O_{u,}\text{out}</td>
<td>2.58–2.68</td>
</tr>
<tr>
<td>O_{u,}\text{out}</td>
<td>88.1–88.8</td>
</tr>
<tr>
<td>O_{v,}\text{out}</td>
<td>90.6–91.4</td>
</tr>
<tr>
<td>O_{u,}\text{in}</td>
<td>91.0–92.3</td>
</tr>
</tbody>
</table>

[a] O_{u,}\text{in}, outer or inner uranyl oxygen atom. U=O_{u,}\text{in}, peroxo-cage oxygen in the hexagonal (H) or pentagonal face (P). [b] Some oxygen positions could not be well-resolved.

was more stable than the C_{3v} isomers; the same result was observed in the orientations of M(O_2)_4 in the X-ray structures of Nb@Rb,K_{12}U_{28},[8] Ta@Cs,K_{12}U_{28}, Nb@Rb,Na_{12}U_{28}, and Ta@Cs,K_{12}U_{28}. No significant effect of the central M atom could be observed (nor did we expect it to because

![Figure 2. Two orientations of M(O_2)_4 inside a tetrahedron that was formed by M sites.](image)

![Table 2. Relative stability (RS) [kcal mol^{-1}] of the D_{3d} isomer versus the C_{3v} isomer, and HOMO-LUMO gap [eV] of the D_{3d} isomer for the M=K,M'=Na;U_{28} nanocapsules.](image)
Ta$^{5+}$ and Nb$^{5+}$ were isovalent and of similar ionic radii), but the cations strongly affected the stability of the $D_{3d}$ isomer. For example, Na-derivatives showed bigger differences between the two isomeric structures, with the Cs/Na system showing the largest difference. The larger stability of the $D_{3d}$ symmetry was attributed to an enhanced interaction between the M(O$_2$)$_4$ guest and the internal alkali metals, as was derived from the computed encapsulation energies with respect to the free fragments [M(O$_2$)$_4$]$^3-$ and M$^+$M$^{12+}$U$_{28}$ (see the Supporting Information, Table S3). In the $D_{3d}$ cage, the peroxo ligands of M(O$_2$)$_4$ formed ideal bond lengths with all 12 M$^+$ cations (2.4–2.5 Å for Na$^+$ and 2.7–2.9 Å for K$^+$). The $C_{3v}$ cage provided analogous peroxide–alkali-metal bonding to only the four M$^+$ cations. We computed quite large energy values, in the range ~60 to ~100 kcal mol$^{-1}$ for all cases. Solvation effects, in part, dominated this energy gain; nevertheless those systems containing sodium showed the largest relative stabilization.

Because of this distortion, there were two non-equivalent positions for the M$^-$=Na or K sites, which precisely corresponded to the two partially occupied sites (2/3, 1/3) in the X-ray structure of Nb@Rb$_4$K$_{12}$U$_{28}$ (twinned small gray spheres, Figure 4, right).[9] The corresponding M$^+$ sites (large purple spheres) did not show such disorder because they were almost perfectly superimposed. In contrast to M$^+$ and M$^-$, the structure of the internal peroxo ligands that belonged to the “yl” and peroxo cage atoms (Figure 5). The total DOS and the projected DOS for the p oxygen IR spectrum. Computed harmonic vibrational frequencies for M(O$_2$)$_4$@Cs$_6$K$_{13}$U$_{26}$ (M=Ta: 837, 518, 487 cm$^{-1}$; M=Nb: 843, 516, 492 cm$^{-1}$) corresponded to the O–O and to M–O bond tensions of the encapsulated M(O$_2$)$_4$ species, which was in very good agreement with the experimental findings.[6]

Electronic structure: The electronic structure of these nanocapsules was quite similar to that of a typical polyoxometalate.[9] Figure 5 shows the total density of states (DOS) and the contribution of uranium and oxygen atoms (projected DOS), as well as a plot of the HOMO and the LUMO for Ta@Cs$_6$K$_{13}$U$_{26}$. The so-called “oxo” band (gray box) was observed from ~10 to ~5 eV, which comprised the symmetry-adapted combinations of the oxygen p electrons, i.e., those that belonged to the “yl” and peroxo cage atoms (Figure 5). The total DOS and the projected DOS for the p oxygen basis set functions (gray shaded areas) indicated that the or-
bitals in the “oxo” band was roughly composed of pure oxygen, with a minor contribution from uranium (projected DOS for uranium f orbitals is the black shaded area). The four π* orbitals of the inner peroxo ligands were observed at around \(-4.5\) eV, the highest of which was actually the HOMO (Figure 5). The lowest empty set of orbitals was made up of the empty f orbitals of the fully oxidized U\(^{VI}\) ions. The first band (\(-3\) eV, narrow black peak) was comprised of precisely 84 energy levels, which arose from the three lowest, almost degenerate, empty molecular orbitals of each \(\text{[UO}_2(\text{O}_2)\text{]}^4^-\) moiety (see the Supporting Information, Figure S4). In this band, and above it, we found uranium f orbitals that were combined with the π* orbitals of the peroxo ligands of the capsule. Combinations of the σ* orbitals of the peroxo ligands of the capsule were at much-higher energies.

As mentioned above, the stability of these nanocapsules was mainly dictated by the alkali cations, much more so than by the central anion. The HOMO–LUMO energy gaps (in Table 2) also pointed in this direction. The two species with Na\(^+\) cations had the largest values, 0.5 eV larger than the O\(^2-\) ions. The data for U@Cs\(_4\)K\(_{12}\)U\(_{28}\) are shown in Figure 6. The principal feature in the negative sweeps was an irreversible wave with a cathodic peak current at \(-0.99\) V (\(E_{pc}\)). This single feature accounted for the scalar value of 81(\(\pm 5\)) electrons: 1) A two-electron reduction of each of the 42 O\(^2-\) ligands would account for 84 electrons, which was within the level of estimated uncertainty of the experimental data. 2) A one-electron reduction of each of the 28 UO\(_2^{2+}\) moieties (into UO\(_2^+\)), which would account for 28 electrons, as well as a simultaneous reduction of a corresponding number (28) of peroxo units, which would account for 56 electrons, would afford an overall 84-electron process that was also consistent with the experimental data. In both scenarios, the reduction of either all (1) or two-thirds (2) of the O\(^2-\) ligands would result in an irreversible breaking of the O−O bonds that are essential bridging groups in the assembly of the spherical structure of U@Cs\(_4\)K\(_{12}\)U\(_{28}\). The loss of color upon reduction and the total number of electrons that were involved in the reduction, as well as the cycle-to-cycle variation of the CV data, were correlated events, thereby suggesting reduction of uranyl(VI) centers and peroxo linkages; the outcome of which was cluster fragmentation. The structural changes that arose from the exhaustive reduction of U@Cs\(_4\)K\(_{12}\)U\(_{28}\) were irreversible; the original yellow color of the solution could not be regenerated by bulk electrolysis at controlled electrode potentials of \(-0.22\) V and higher. The bleaching of the yellow color was consistent with the reduction of U\(^{VII}\) into U\(^{V}\) in alkaline solution, as has been observed previously. To the degree...
that the color bleaching indicated that the \( \text{UO}_2^{2+} \) moieties were electrochemically involved in the reduction, this result is consistent with the theoretical results. Indeed, these calculations for \( \text{M}^+\text{M}'\text{M}''\text{M}'''\text{U}_{28} \) showed that the first LUMO band was cage-centered and was formed from exactly 84 levels, which were mainly comprised of uranium 5f orbitals with a non-negligible contribution of O–O π-antibonding character. This result was in line with the redox chemistry of mononuclear uranyl(VI)–peroxo complexes, such as \( [\text{UO}_2\text{O}_2\text{O}_3]^{3-} \), in alkaline hydroxide electrolytes.\(^{[10,11]} \)

In the positive-going cycles, there were small irreversible waves with anodic peak currents in the range \(-0.66\) to \(-0.62 \, \text{V} (E_{pa})\), which were correlated with the \( E_{pa} \), and a small, quasi-reversible couple with a half-wave potential \((E_{1/2})\) of \(-0.14\) to \(-0.12 \, \text{V} \) near the high-limit switching potential. This quasireversible process was attributed to the oxidation of the innermost peroxo ligands; the removal of electrons from the peroxo-based HOMOs would lead to the formation of a superoxo complex that would be prone to disproportionation were it not stabilized by uranyl(V), as in calculations reported previously.\(^{[12]} \) In so far as the difference between the applied electrode potentials for the first reduction \((E_{pa} = -0.99 \, \text{V})\) and the first oxidation \((-0.14 \leq E_{1/2} \leq -0.12 \, \text{V})\) provided an electrochemical measure of the HOMO–LUMO gap,\(^{[13]} \) the experimental value of 0.9 V compares favorably with the calculated values (Table 2). Moreover, the calculated band-gap of \( \text{U} \)@\( \text{NaRbU}_{28} \) (1.1 eV) matches the value observed by electrochemical analysis. An investigation towards a full description of these uranyl-centered \( \text{U}_{28} \) nanocapsules is underway.

**Conclusion**

The molecular structures of the \( \text{M} \)@\( \text{M}'\text{M}''\text{M}'''\text{U}_{28} \) (\( \text{M} = \text{Nb}, \text{Ta} \); \( \text{M}' = \text{Rb}, \text{Cs} \); \( \text{M}'' = \text{Na}, \text{K} \)) systems were fully determined by DFT-based methods and agreed perfectly with the X-ray data for \( [\text{Ta} \text{O}_2]@\text{CsNa}_6\text{U}_{28} \) and \( [\text{Nb} \text{O}_2]@\text{RbNa}_6\text{U}_{28} \) and with related systems that were recently characterized by experiment.\(^{[6]} \) In all cases, the most-stable structure had \( D_{2d} \) symmetry. The Na and Cs cations that were trapped inside the capsules provided the largest enhancement in stability, whereas tetraperoxides (Nb or Ta) only had a minor effect. The origin of the crystallographic disorder was explained on the basis of the computed structures. The 84-electron reductive decomposition of \( \text{U}_{28} \) with an electrode that was polarized at \(-1.300 \, \text{V} \) included the reduction of the uranium centers and the breaking of (peroxo) O–O ligand bonds, also by reduction.

We obtained a remarkable agreement between experimental and theoretical data, which fully described the electronic and structural features of uranyl–peroxo polyoxometalate (POM)-like nanocapsules. Like classic transition-metal POMs, structural stability could be achieved based on the association or encapsulation of cations. Despite the apparent similarities between the electronic structures of POMs and actinide–peroxo clusters, their electrochemical behaviors stand in sharp contrast. Whereas the former clusters are renowned for their reversible electrochemistry and the formation of heteropoly blues, the latter systems cannot undergo electrochemical reduction without destruction of the peroxide ligands that hold the clusters together. The insight gained from these studies presents a significant synthetic challenge: the rigorous elimination and replacement of the peroxide ligands with alternatives that both provide curvature for cluster formation—like the peroxide ligands—yet are stable under electrochemical reduction.

### Experimental Section

**Computational details:** All of the calculations were carried out with the ADF program system, version 2010.01, which was developed by Baerends, Ziegler, and co-workers.\(^{[14]} \) We used a density functional theory (DFT)-based method, which included the local VWN exchange-correlation potential\(^{[15]} \) with the GGA exchange correction reported by Becke\(^{[18]} \) and the correlation correction reported by Perdew\(^{[19]} \) (BP96). A triple-\( \zeta \) plus-one polarization function basis set was used on all atoms by treating the core electrons with a relativistic frozen-core potential. Relativistic corrections were introduced by using a scalar-relativistic zero-order regular approximation (ZORA).\(^{[20,21]} \) Solvent effects were introduced by using the continuous solvent model COSMO\(^{[22,23]} \) with standard parameters for water and the atomic radii reported by Klamt et al.\(^{[24]} \) These derivatives were evaluated by using the Mobile Block Hessian (MBH) method,\(^{[22,23]} \) from which a partial Hessian matrix was computed. All of the Hessian eigenvalues were positive.}

**Synthesis and crystallography of \( \text{Ta} \)@\( \text{M} \)@\( \text{M}'\text{M}''\text{M}'''\text{U}_{28} \) and \( \text{Nb} \)@\( \text{M} \)@\( \text{M}'\text{M}''\text{M}'''\text{U}_{28} \):** The synthesis and crystallographic analysis of \( \text{Ta} \)@\( \text{M} \)@\( \text{M}'\text{M}''\text{M}'''\text{U}_{28} \) and \( \text{Nb} \)@\( \text{M} \)@\( \text{M}'\text{M}''\text{M}'''\text{U}_{28} \) have been reported previously.\(^{[6]} \) These \( \text{U}_{28} \) analogues with \( \text{M} \)@\( \text{M}'\text{M}''\text{M}'''\text{U}_{28} \) (\( \text{M} = \text{Nb}, \text{Ta} \) in the center of the capsule, \( K^+ \) in the pentagonal rings, and \( \text{Rb} \) or \( \text{Cs} \) in the hexagonal rings) is rapidly degraded if left in the cold, but it is stable at ambient temperature. A synthesis that is crucial for obtaining good X-ray data, in that the quality of the crystal rapidly degraded if left in the oil for an extended time, perhaps owing to loss of water. Single-crystal X-ray diffraction data were collected at 180 K on a Bruker AXS SMART-CCD diffractometer with graphite-monochromated Mo K\( \alpha \) (0.71073 \, \text{Å} \) radiation. Data collection and reduction were carried out with the SMART 5.043 (Bruker, 1998) and SAINT 6.02 (Bruker, 2001) software packages, respectively. Numerical absorption correction from face indexing was applied. The structures were solved by direct methods (program SIR97) and refined by full-matrix least-squares on \( F^2 \) (SHELX97). All subsequent structure solutions and refinements were performed with the WinGX system. The identity of the cations (\( \text{Na}^+ \) and \( K^+ \) were optimized by a combination of the alkali-metal–oxygen bond length and coordination geometry, thermal parameters, and energy-dispersive spectroscopy (EDS).

**Electrochemistry of \( \text{U} \)@\( \text{NaM}_{12}\text{U}_{28} \):** All electrochemical measurements were performed at ambient temperature on a BASi 100B/W electrochemical workstation. Cyclic voltammetry (CV) data were obtained in a single-compartment glass cell by using a 1.6 mm diameter gold disc working electrode (BASi, model MF-2014) and a Ag/AgCl reference electrode (3 mol \( \text{NaCl} \) that had a porous Vycor tip (BASi, model MF-2025), against which all potentials are quoted, unless otherwise stated. A

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To determine the electron count from the coupled chemical reactions. The most-pronounced variations occurred in the CV of \( \text{U@Cs}_4\text{K}_{12}\text{U}_{28} \). Most notably, in alkaline solution, the peroxoanions \((\text{O}_2^-)\) were readily reduced to two electrons into hydroxo ions \((\text{OH}^-)\) with a standard electrode potential of \(-0.867 \text{ V versus SHE}\). Similarly, in alkaline solution, \(\text{O}_2^-\) was readily oxidized into superoxo \((\text{O}_2^2-)\) and its possible oxidation. High-quality CV data were acquired for fresh solutions of \(\text{U@Cs}_4\text{K}_{12}\text{U}_{28}\). In Figure S5, the electrochemical oxidation of \(\text{U@Cs}_4\text{K}_{12}\text{U}_{28}\) was performed in an identical fashion with the neat supporting electrolyte. Experiments were performed with fresh samples at a continuous \(\text{N}_2\) sparge (and magnetic stirring) throughout the course of the electrolysis. A Journey inside the \(\text{U}_28\) Nanocapsule

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[8] Further details of the crystal structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html) or from the International Center for Diffraction Data, Newtown Square, Pennsylvania 19073, USA (fax: (+1) 610-528-2909; e-mail: icdd@icdd.com).

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