The High Pressure Response of Uranyl Nano-Cages: Insights on the Roles of Chemistry and Cluster Topology

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Hexavalent uranium self-assembles into nano-cages in the presence of peroxide solutions. These clusters consist of 20 to 68 uranyl (UO_2^{2+}) units. Although over 80 unique clusters have been described, there has been no investigation of the response of different cluster topologies to elevated pressures. In the present work, the responses of two nano-cages, {U_{60}} and {$U_{24}Py_{12}$}, were studied *in situ* at extreme pressures, up to 17 and 50 GPa, respectively. {U_{60}} clusters are topologically identical to carbon fullerenes, forming isometric crystals with the formula: $Li_{68}K_{12}(OH)_{20}[UO_2(O_2)(OH)]_{60}(H_2O)_{310}$. In diamond anvil cell (DAC) experiments, the fullerene {U_{60}} topology is stable up to pressures of 10 GPa, above which the structure collapses irreversibly. A pressure-induced tetragonal structure (*a* = 36.6764(2), c = 35.1672(4) Å) forms in the range of 4 to 10 GPa, as determined by *in situ* synchrotron XRD and confirmed by Raman spectroscopy. At pressures above 10 GPa, the {U_{60}} decomposes into smaller macromolecules of {U_{10}}, {U_{15}}, and {U_{20}}. {$U_{24}Py_{12}$} clusters form tetragonal crystals at ambient pressures with the formula: $Na_8[(UO_2)_{24}(O_2)_{24}(P_2O_7)_{12}]$. Single crystals of {$U_{24}Py_{12}$} undergo reversible pressure-induced amorphization at 17 GPa. Based on Raman spectroscopy, the uranyl units persist up to 50 GPa. Following pressure quenching, the original tetragonal structure of {$U_{24}Py_{12}$} recovers, as evidenced by *in situ* XRD and Raman spectroscopy. In contrast to the topologically-identical C_{60}, which collapses at pressures above 30 GPa, but retains its hexagonal structure, {U_{60}} loses its long-range periodicity at much lower pressures and ultimately forms smaller clusters. {$U_{24}Py_{12}$} retains its chemical and structural integrity upon pressure quenching. The persistence of these uranyl nano-cage structures both during and after the application of high pressure suggests that the uranyl nano-cage structures are very stable, once formed.