

Oxidation State Assignment in Cerium Nanoclusters: Conflicting Conclusions from Single Crystal X-ray Diffraction and Spectroscopic Data

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Over the last decade, ceria nanoparticles have received much attention as an alternative to bulk cerium dioxide (CeO₂) due to their increased reactivity at lower temperatures. Further interest in Ce based clusters and nanoparticles stems from the nuclear community as cerium has historically been used as a surrogate for plutonium owing to their similar ionic radii, similar coordination environments, and accessible 3+/4+ redox couples. Several cerium clusters have been isolated using organic capping ligands to passivate the surface, thereby halting further oligomeric growth. Clusters capped by inorganic ligands, such as Cl⁻, are a bit more elusive. Yet our group has recently harnessed nonbonding interactions to isolate several Ce nanoclusters capped by chloride ions and water molecules; however, the valence state assignment of the Ce sites and the μ₃-O/OH sites on the cluster surface remains unclear. In one such example, we have crystallized a compound whose structure is built from Ce₃₈ clusters. Analysis by single crystal X-ray diffraction and bond valence summation point towards exclusively tetravalent cerium but there is ambiguity in the assignment of μ₃-O/OH sites and the occupancy of outer sphere cations that charge balance the clusters, both of which have implications on the Ce oxidation state assignment. Additionally, other experimental data including X-ray absorption and X-ray photoelectron spectroscopies suggest the presence of Ce³⁺ in the cluster; charge compensation of the Ce⁴⁺/Ce³⁺ ratio can be accounted for through the relative ratio of μ₃-O/OH surface sites. Several plausible formula for the clusters have been determined. Taking into account both the SCXRD and spectroscopic data, “would you publish this”?