

Phosphorus-based ligand effects on the structure and radical scavenging ability of molecular nanoparticles of CeO₂

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Two new Ce^{IV}/O²⁻ clusters, (pyH)₈[Ce₁₀O₄(OH)₄(O₃PPh)₁₂(NO₃)₁₂] (**1**) and [Ce₆O₄(OH)₄(O₂PPh₂)₄(O₂C^tBu)₈] (**2**), have been prepared that contain P-based ligands for the first time. They were obtained from the reaction of (NH₄)₂[Ce(NO₃)₆], PhPO₃H₂ or Ph₂PO₂H, and ^tBuCO₂H in a 212 molar ratio in pyridine/MeOH (101 mL). Both compounds contain a {Ce₆O₄(OH)₄} face-capped octahedral core, with **1** containing an additional four Ce^{IV} on the outside to give a supertetrahedral Ce₁₀ topology; the {Ce₆O₈} unit is the smallest recognizable fragment of the fluorite structure of CeO₂. The HO[•] radical scavenging activities of **1** and **2** were measured by UV/vis spectral monitoring of methylene blue oxidation by HO[•] radicals in the presence and absence of the Ce/O clusters, and the results compared with those for larger Ce₂₄ and Ce₃₈ molecular nanoparticles of CeO₂ prepared in previous work. **1** and **2** are both very poor HO[•] radical scavengers compared with Ce₂₄ and Ce₃₈, a result that is consistent with reports in the literature that PO₄³⁻ ions inhibit the radical scavenging ability of traditional CeO₂ nanoparticles and putatively assigned to PO₄³⁻ binding to the surface.

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