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Formation and structure of polynuclear tetravalent actinide and lanthanide carboxylates in aqueous solution and solid state

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Tetravalent actinides and lanthanides form strong complexes with carboxyl containing ligands. Such complexes play an important role in technological processes as well as in biological and environmental systems. So far, most of the thermodynamic data of actinide(IV) and lanthanide(IV) carboxylates are estimated by assuming mononuclear solution species [1]. We applied comprehensive studies with EXAFS, UV-Vis-NIR spectroscopy and X-ray diffraction on Th⁴⁺, U⁴⁺, Np⁴⁺ and Ce⁴⁺ carboxylates (RCOO⁻; R = H, CH₃, CHR'NH₂; R' = H, CH₃, CH₂SH) in aqueous solution and solid state [2-5]. Our studies reveal that in all of the investigated systems hexanuclear complexes appear, which become predominant with increasing metal and ligand concentration and increasing pH, and dominate finally the species distribution. We present here their structure, stability constants, and the mechanisms of complex formation. The appearance of hexanuclear complexes in aqueous solution coincides with the onset of the An(IV) hydrolysis on the one hand, and the deprotonation of the carboxylic function on the other hand. This results in a competing reaction between hydrolysis and ligation. The hydrolysis induces a polymerization of the metal ions via oxo and hydroxo bonds, whereas 12 carboxylic ligands provide charge neutrality of the hexanuclear core and prevent further polymerization. Our studies indicate that future work on tetravalent actinide carboxylates in aqueous solution requires consideration of these hexanuclear species.

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