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Structures of hydrated and hydrolyzed thorium(IV) determined by EXAFS and LAXS

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The hydrated thorium(IV) ion is nine-coordinate in strongly acidic aqueous solution with a mean Th-O bond distance of 2.45(1) Å as determined by extended X-ray absorption fine structure (EXAFS) and large angle X-ray scattering (LAXS) [1]. The presence of a second hydration sphere was indicated by LAXS with cca 18 water molecules at 4.66(2) Å. Structural studies in aqueous solution of the hydrolysis products of thorium(IV) identified three different types of hydrolysis species: a μ_2 -O-hydroxo dimer, $[\text{Th}_2(\text{OH})_2(\text{H}_2\text{O})_{16}]^{8+}$, a μ_2 -O-hydroxo tetramer, $[\text{Th}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8+}$, and a μ_3 -O-oxo hexamer, $[\text{Th}_6(\text{O})_8(\text{H}_2\text{O})_n]^{8+}$. Strongly acidic solutions are required to stabilize the hydrated thorium(IV) ion. With increasing concentration and pH thorium(IV) hydrolyzes, first, to a dimer with double hydroxo bridges, then to a tetramer with the thorium(IV) ions forming a diamond (represented by two dimers merged together) [1]. Finally, at pH value close to precipitation of thorium(IV) oxide/hydroxide, a hexamer is formed with the thorium atoms forming a rhombicuboctahedron. Potentiometric studies suggested a hexamer composition $[\text{Th}_6(\text{OH})_x(\text{H}_2\text{O})_n]^{x-}$, $x = 14$ or 15 [2]. However, the rhombicuboctahedral structure prevents for sterical reasons such a large number of hydroxide groups to be bound. Instead 7-8 oxo groups are bound to thorium ions as from proton activity point of view 16 hydroxo groups are equivalent to 8 oxo groups, making it impossible to distinguish between e.g. $\text{Th}_6(\text{OH})_{16}^{8+}$ and $\text{Th}_6\text{O}_8^{8+}$ complexes. A compilation of reported solid state structures of actinoid(IV) compounds with oxygen donor ligands show a strong correlation between the An-O bond distance and the coordination number [1]. EXAFS studies of uranium(IV), neptunium(IV) and plutonium(IV) ions in aqueous solution have reported accurate An-O bond distance, but the coordination numbers were less accurate and often overestimated. The hydrated tetravalent actinoid ions in aqueous solution all seem to be nine-coordinated [1].

References:

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