

The electronic structure of uranyl and neptunyl carboxylates

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Chemical bonding in actinyl complexes attracts a wide interest due to its uniqueness and complexity. Indeed, electrons of highest shells are not distributed uniformly around an actinide atom. According to literature, the electrons of highest shells form localization domains, their shape most likely defined by the nature of bonding atom and actinide itself¹⁻³. These localization domains cannot be easily associated with the particular valence shells.

In present thesis we report the results of experimental and quantum chemical studies of three carboxylate complexes of uranyl and neptunyl: Cs[$\text{UO}_2(\text{C}_3\text{H}_7\text{COO})(\text{OH})(\text{H}_2\text{O})$][$\text{UO}_2(\text{C}_3\text{H}_7\text{COO})_3$] (**1**), $\text{AcO}_2(\text{OOC}(\text{CH}_2)_2\text{CH}_3)_2(\text{H}_2\text{O})_2$ (Ac = U (**2**), Np(**3**)). The crystal structures of isostructural complexes **2** and **3** were obtained by high resolution single crystal X-ray diffraction. The structure of **1** was established by combination of powder X-ray diffraction and quantum chemical calculations utilizing plane wave basis set. Chemical bonding in **1-3** was analyzed in terms of topological analysis of electron density and ELF functions.

The structure of **1** can be described as coordination polymer and it contains two uranium atoms with different coordination numbers (CN = 7 and 8). The atomic charges of these uranium atoms in the structure **1** are slightly different (3.31 and 3.39 e) that is somewhat larger than charge of uranium in isolated UO_2^{2+} (3.20 e). On the contrary, for the complexes **2** and **3** the discrete structure was found. Uranium(VI) and neptunium(V) atoms have the same coordination environment, but their Bader charges considerably differ (2.98 and 2.83 e).

Analysis of ELF function demonstrated the presence of extensive maxima (localization domains, Fig. 1) attributed mostly to 6s and 6p electrons. The number and the position of localization domains are related to the electron withdrawing effect of the bonding atom (ligand). In all complexes studied the localization domains are directed towards the ligand with lowest electron-withdrawing effect (H_2O) or located between carboxylic groups.

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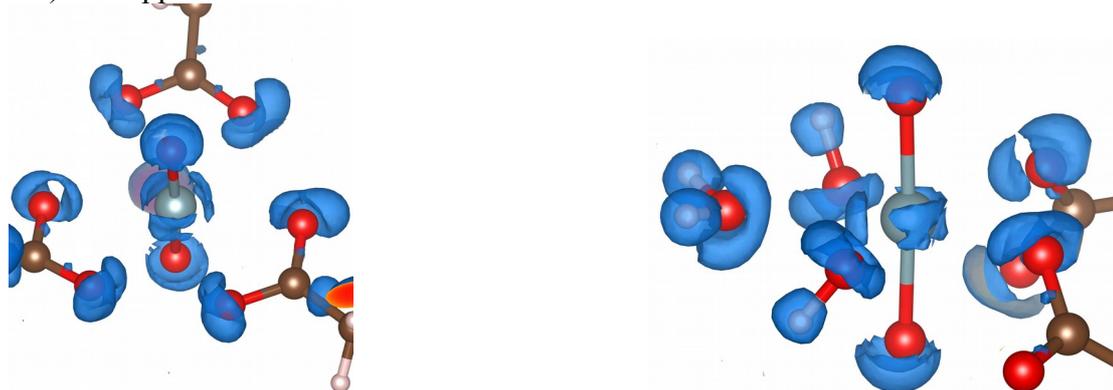


Figure 1. 3D isosurface of ELF function (0.85) illustrating the position of maxima correspond to valence electron around U1 (left) and U2 (right) atoms in **1** versus electron pairs localized near adjacent oxygen atoms.

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