

Synthesis and characterization of chiral thorium(IV) and uranium(IV) benzamidinate complexes

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Two chiral benzamidinate complexes of tetravalent actinides (Th(IV) and U(IV)) were synthesized using a salt metathesis reaction of the corresponding actinide(IV) tetrachlorides and the potassium salt of the chiral benzamidinate ((S,S)-N,N-Bis-(1-phenylethyl)-benzamidinate ((S)-HPEBA). The structure of the complexes was determined with single crystal X-ray diffraction. These are the first examples of chiral amidinate complexes of actinides.

Oxygen- and nitrogen-donor ligands are known to form stable complexes with actinides, which could potentially influence the migration behavior of these radioactive elements in a nuclear waste repository. Therefore, the understanding of the interaction mechanisms between actinides and these types of ligands would be crucial for the safety assessment of the waste repository. Based on this background, the present study focuses on the interaction of actinides with a benzamidinate ligand, which can be considered as a model of naturally occurring N-donor organic compounds. Furthermore, due to its chemical similarity to the relevant O-donor ligand of carboxylic acids, the comparison between these two major strong ligands is of particular scientific interest. The advantage to use amidinates is the possibility to tune the electronic properties on the donating atoms (i. e. coordinating N atoms) as well as steric properties by varying the substituents. Interestingly, only a limited number of chiral metal complexes with benzamidinates has been reported so far. Recently, the group of P. Roesky has shown an effective synthesis route for the chiral benzamidinate ((S,S)-N,N-Bis-(1-phenylethyl)-benzamidinate ((S)-HPEBA) and the corresponding potassium salts,^[1] and have successfully synthesized some lanthanide complexes with this chiral benzamidinate.^[2] The present study is inspired by these precedent studies to synthesize new benzamidinate compounds of tetravalent actinides, Th(IV) and U(IV).

EXPERIMENTAL. All preparations and syntheses were performed in a water-free N₂-filled glovebox and standard Schlenk techniques. All solvents were distilled from Na/K alloy and stored over molecular sieve 4 Å. ThCl₄(DME)₂,^[3] UCl₄,^[4] and (S)-KPEBA^[1] were prepared according to the standard procedures reported in the literature.

RESULTS. The synthesis route for the complexes [ThCl((S)-PEBA)₃] (**1**) and [UCl((S)-PEBA)₃] (**2**) is shown in Fig. 1.

The salt metathesis reaction can be easily monitored by a color change of the sample solution (toluene) from colorless

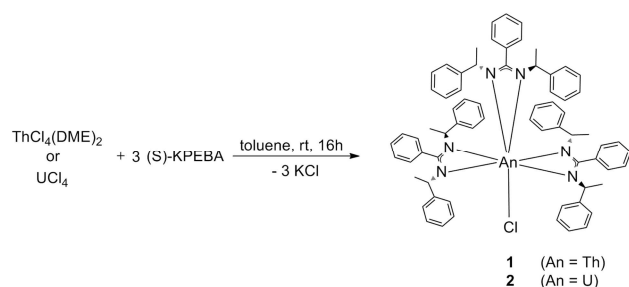


Fig. 1: Synthesis of [ThCl((S)-PEBA)₃] (**1**) and [UCl((S)-PEBA)₃] (**2**).

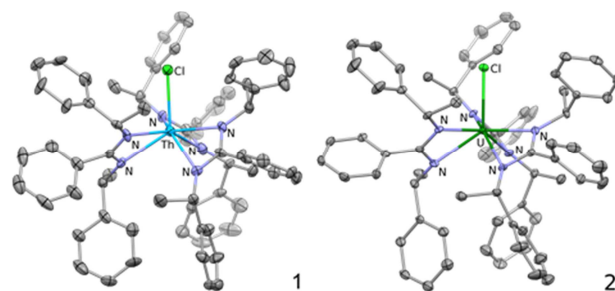


Fig. 2: Molecular structures of [ThCl((S)-PEBA)₃] (**1**, left) and [UCl((S)-PEBA)₃] (**2**, right).

to pale green, whereas the potassium chloride precipitates as an off-white solid.

Single crystals of complexes **1** and **2** were obtained by filtration of the resulting suspension, drying *in vacuo*, and recrystallization from a toluene/*n*-pentane solution. The crystal structures of the obtained single crystals were determined by single crystal X-ray diffraction. The determined molecular structures of **1** and **2** are shown in Fig. 2.

The Th(IV) and U(IV) complexes are isostructural with three benzamidinate ligands coordinating to the actinide(IV) cation. Additionally, one chloride (Cl⁻) is bound to the actinide center resulting in the monocapped distorted octahedral coordination sphere. All three benzamidinate ligands are coordinating to the metal center asymmetrically and the tilt angle between the plane consisting of the coordinating N-C-N atoms of the amidinate ligand and the An-Cl axis varies within the three ligands from 40.22° to 50.44°. Due to the steric hindrance of the bulky amidinate ligands, no symmetrical coordination was observed in the obtained complexes. The averaged U-N bond length in **2** (2.43 Å) is slightly shorter than the Th-N bond length in **1** (2.49 Å) due to the actinide contraction.^[5]

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