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## 5f electron polarizability in a full early actinide (Th-Pu) pyren complex series

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In contrast to the strongly shielded 4 *f* electrons of the lanthanides, 5 *f* electrons of particularly the early actinides are found to participate in bonding, e.g. to organic ligands. Reactivity and complexation strength of such bonds are the most influenced by donor properties of the ligand and the electronic situation of the actinide metal center. Furthermore, coinciding properties of ligand and actinide ion regarding *Pearson's* principle of hard and soft acids and bases (HSAB) can even drive the development of selective ligands, e.g. for extraction processes. Here, soft *N*-donor ligands were found to interact stronger with trivalent actinides in comparison to their harder lanthanide analogues.

To evaluate how these HSAB properties can be extended to a series of tetravalent actinides and their interactions with *N*-donor ligands, we have studied the complexation of tetravalent Th, Pa, U, Np, and Pu with *N,N'*-ethylene-bis((pyrrole-2-yl)methanimine (pyren) in comparison to its structural *N, O*-analogue, the salen ligand.

Complex syntheses using one equivalent of  $AnCl_4(dme)_x$  (*An* = Th, U, Np, Pu; *x* = 0 for U, *x* = 2 for Th, Np, Pu) and two equivalents of pyren led to isostructural 2:1 complexes, which were analyzed in the solid state by SC-XRD and IR, as well as in solution via NMR spectroscopy. SC-XRD results and quantum chemical calculations revealed differences in *An*<sup>IV</sup>-ligand bond length and strength within pyren (*N*-imine vs. *N*-pyrrolide donors) or salen (*N*-imine vs. *O*-phenolate). Interestingly, the overall bond strength of the *N*-donor vs. *N, O*-donor to *An*(IV), however, is almost equal for both,  $[An(pyren)_2]$  and  $[An(salen)_2]$  (*An* = Th-Pu). Delocalization indices even confirmed slightly more covalent interactions between the *N, O*-donor salen and Th, U, Np, and Pu in comparison with pyren. For Pa, on the other hand, this trend is reversed. QTAIM analysis could prove particularly strong interactions with the pure *N*-donor ligand pyren. This extraordinarily good electron sharing between pyren and Pa can be explained by the 5 *f*<sup>1</sup> configuration of Pa(IV), being particularly well polarizable and thus well suited for an effective backbonding to the soft *N*-donors of the pyren ligand.

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