A short retrospective of actinide hexacyanoferrate exploration initiated at LURE

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ABSTRACT

The occurrence of actinide elements is related to the production of nuclear energy. But actinide elements are also interesting for their specific chemistry, largely due to their position at the bottom of the periodic Table and the occurrence of the *5f* orbitals in their electronic configuration. It is in the late 90s that synchrotron tools were used to investigate the speciation of actinide molecular compounds. The first article dealing with the speciation of plutonium with EXAFS goes back to 1993 with data recorded at SSRL.[1]

The formation of a metal-ligand coordination bond is most often described as resulting from the use of a free electron pair around a ligand atom. The coordination chemistry of the actinides, although less well-developed than that of the *3d*, *4d*, and *5d* metals, is quite distinctive. In contrast, the lanthanide series, often presented as analogous since it also contains *f*-valence orbitals, exhibits only one stable oxidation state (with a few exceptions) and primarily ionic cation-ligand interactions.

In 1996-97 at CEA Marcoule was launch a program to study actinide molecular chemistry with X-ray Absorption techniques and this was initiated experimentally at D44 of LURE. One system of interest was the well-known Prussian Blue family of molecular edifices because they were studied for a long time with transition metals. Although the geometry of the hexacyano-metalate brick is very rigid and the octahedral geometry is favoured for both metal sites, different types of structures can be observed depending on the synthesis conditions. As a study case of fundamental actinide chemistry, we chose to combine the hexacyanoferrates entities $[Fe^{III}(CN)_6]^{3-}$ and $[Fe^{II}(CN)_6]^{4-}$ (respectively ferricyanide and ferrocyanide ions) as ligands with actinide and lanthanide cations at oxidation states III and IV.[2] These $\{Fe(CN)_6\}$ entities, of rigid octahedral geometry have indeed the ability of forming bonds with a lot of cations by the way of the six terminal nitrogen atoms from the cyano ligands, the later becoming thus bridging. It appears that actinide(IV) compounds exhibit absorption spectra similar to those of hafnium ferrocyanide and significantly different from those of lanthanide ferrocyanides. In particular, the data recorded at the K-edge values for carbon and nitrogen indicate significant overlap between the valence orbitals of the actinides (or hafnium) and the π* orbitals of the cyano ligand.[3] For actinide(III) like americium or californium, analogy can be drawn with neodymium and gadolinium respectively.

REFERENCES

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