



Experiment title: Structure of Protactinium(V) carboxylate and polyaminocarboxylate complexes

Experiment number:
CH-4823

Beamline: BM20	Date of experiment: from: 18/02/17 to: 21/02/17	Date of report: 20/07/2017
Shifts: 9	Local contact(s): Christoph Hennig	<i>Received at ESRF:</i>

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Report:

EXAFS measurements were performed in fluorescence mode using a Si(111) double-crystal monochromator on the Rossendorf Beamline (BM20). Pa(V) and U(VI) samples have been analysed. Data were acquired at Pa L_{III} edge (16733 eV) and U L_{III} edge 17166 eV, respectively.

Unlike the other actinides U, Np, Pu that exhibit a linear trans dioxo bond in their higher oxidation states, Pa(V) species in aqueous solution, has been proved to possess one single oxo bond (in concentrated H₂SO₄, in oxalic acid) or no oxo bond in HF 0.5 M, based on experiments previously performed at ESRF.

This experiment was performed with the aim of getting further information about the structure and the coordination of protactinium (V) as well as of U(VI) in the presence of organic ligands. Some of the complexing agents used in experiment CH-4823 are presented below.

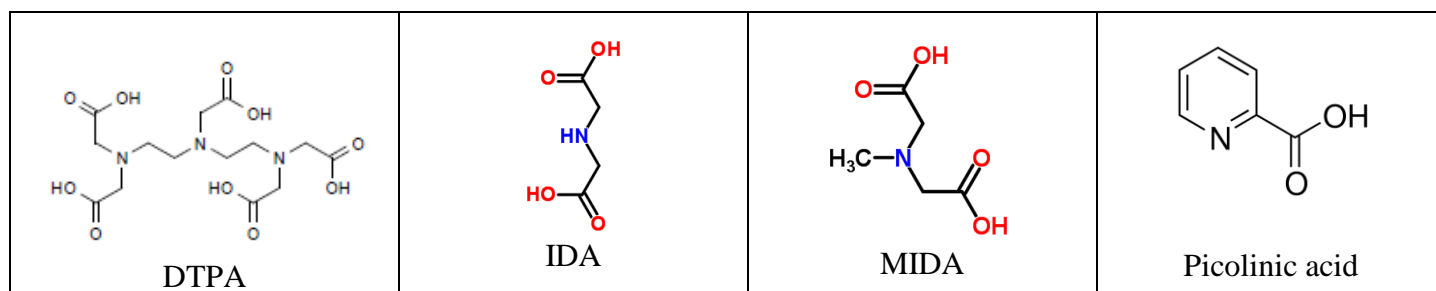


Figure 1 presents the experimental and fitted Pa L_{III} edge EXAFS spectra and the associated modulus of the Fourier transform (FT) of the sample Pa/DTPA. Even if the coordination polyhedra of protactinium in the complex Pa-DTPA is still to be determined, preliminary analysis tend to indicate the absence of the short mono-oxo bond. This result agrees with our previous thermodynamic study of the complexation of Pa(V) with DTPA (Inorg. Chem. (2013) 52 7497-7507).

The data collected on the complexes Pa-IDA (iminodiacetate), Pa-MIDA (methyliminodiacetate) and Pa-Cit (citrate) have led to the same conclusion: no mono-oxo bond was observed. Preliminary theoretical calculations on Pa-IDA system state indeed that complex with the “PaO” moiety is not stable.

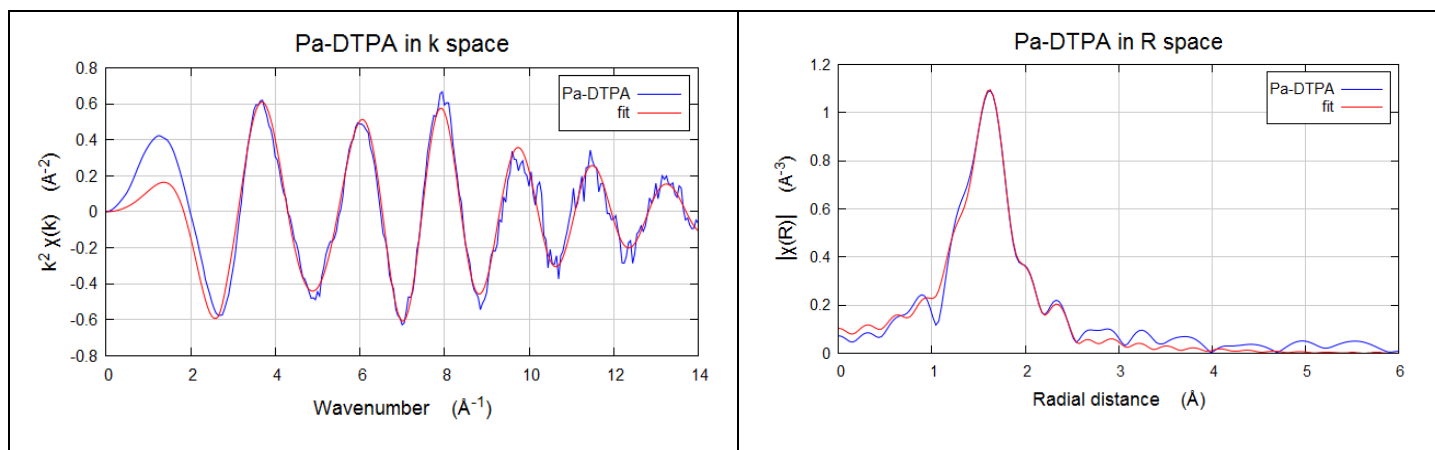


Figure 1: EXAFS spectra and FT of Pa(V) $2 \cdot 10^{-3}$ M in the mixture 0.05 M DTPA and 3 M HCl

The preparation of the sample U(VI)-picolinate (2-pyridine-carboxylate) in the stoichiometry 1:1 was difficult due to the precipitation of the complex 1:2 as soon as the ratio ligand/U reaches a value higher than 1. The sample analyzed in the present experiment has been proved to be stable over 4 months. The pyridine nitrogen atom is expected to favour the chelation of U(VI) with a possible formation of a 5-membered ring. In figure 2, the first peak corresponds to two axial oxygen atoms (O_{ax}) in a distance of 1.771 Å. The second peak comprises the atoms in the equatorial shell (O_{eq}). The fit reveals an average distance of 2.428 Å and a coordination number of 2.9. However, this coordination number does not correspond with a reasonable coordination geometry. This can be originated either from experimental problems (non homogeneous sample) or structural effects leading to destructive interferences of the individual scattering contribution. Further studies are under way.

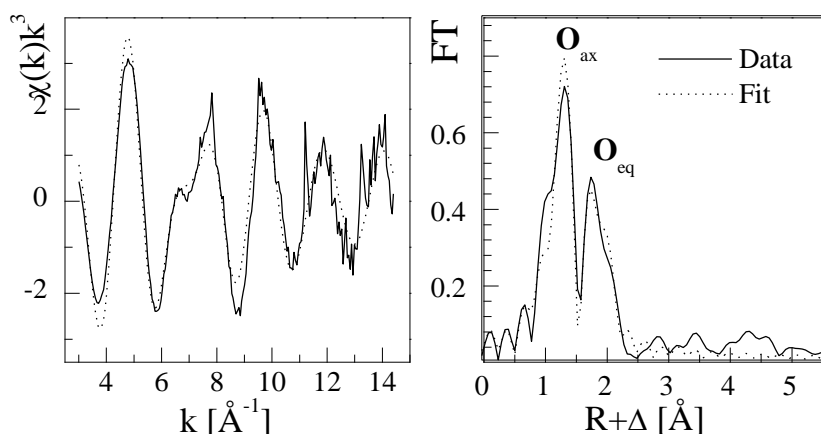


Figure 2: U L₃-edge k^3 -weighted EXAFS data (left) and the corresponding Fourier transform (right) of a solution of 0,095 M U(VI) with 0,09 M picolinic acid and 0.1M HClO₄.