Electronic Supporting Informations : Electronic structure of f-element Prussian Blue analogs determined by soft X-ray absorption spectroscopy.

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1: P.B.A. Synthesis:

AnIV/FeII compounds were synthesized by precipitation/crystallization upon the addition of solutions of ferro- or ferricyanide ions and actinide ions in acidic media (ThIV/FeII, NpIV/FeII, PuIV/FeII, UIV/FeII, CeIII/FeII, NdIII/FeII and EuIII/FeII) The following starting compounds, K_4 [Fe^{II}(CN)₆] $3H_2O$, CeCl₃ $7H_2O$, EuCl₃ $6H_2O$ and NdCl₃ $6H_2O$ were commercially purchased (Aldrich) and used without further purification. Th(IV) solution was prepared ad hoc from the required amount (see below) of purified nitrate compound Th(NO₃)₄, $5H_2O$ from CEA stock in 0.2 M HCl. U(IV) is obtained from uranium tetrachloride prepared in anoxic condition. Np(IV) solution was obtained by reduction of Np^VO²⁺ after dissolution of NpO₂(OH).nH₂O CEA stock with an excess of hydroxylammonium chloride in 2.4 M hydrochloric acid. This stock solution was characterized by UV-vis spectroscopy to check the final neptunium concentration and the absence of NpV contamination: [NpIV] = 0.15 M; [HCI] = 2.4 M. PuIV was directly taken from the referenced CEA stock solution with [PuIV] = 1.5×10^{-2} M in 1 M HNO₃.

All the Pu and Np solutions were handled in radiological glove boxes. The Th solutions were handled in a dedicated fume hood.

- Th^{IV}/Fe^{II} was obtained by mixing a solution of Th^{IV} (21.9 mg of Th(NO)₄,5H₂O in 2 mL of 0.2 M HCl) to an equimolar solution of K₄[Fe^{II}(CN)]₆ (19.9 mg of K₄[Fe^{II}(CN)]₆ also in a 0.2 M HCl solution). The white precipitate was separated from the solution by centrifugation, washed with water (3 times), ethanol and acetone and then dried at room temperature. During these steps the white precipitate slowly turned to a light-blue powder indicating very slight Prussian blue contamination. Hence the synthesis was repeated shortly before characterization (6 hours) and Prussian blue contamination was then check using the iron L₃ edge measurement (absence of Fe^{III} pre-edge features at about 706-707 eV).
- U^{IV}/Fe^{II} is an air sensitive compound. Hence it was prepared in an anoxic glovebox in order to avoid
 U^{IV} oxidation into UO₂²⁺ as observed in first attempts under oxygen conditions.¹ The UIV/FeII

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compound is obtained by mixing a solution of U^{IV} (67 mg of UCl₄ in 1 mL of 0.5 M degazed HCl) to an equimolar solution of $K_4[Fe^{II}(CN)]_6$ (72 mg of $K_4[Fe^{II}(CN)]_6$ in a 0.5 M degazed HCl solution). The green precipitate was separated from the solution by centrifugation, washed with degazed water (3 times) and with dried THF. The final compound is then dried at room temperature. During these steps, and sample preparation the compounds were maintained under annoxide conditions. Prussian blue contamination was then check using the iron L₃ edge measurement (Fe^{III} pre-edge features at 707.5 eV indicates a partial side forms Prussian Blue produced during synthesis and sample preparation).

- Np^{IV}/Fe^{II} was obtained by mixing a solution of Np^{IV} (0.1 mL of the Np^{IV} stock solution diluted in 0.9 mL of 2 M HCl) with an equimolar ferrocyanide solution (8.8 mg of K₄[Fe^{II}(CN)]₆ diluted in 1 mL of a 0.2 M HCl solution). The dark red precipitate was separated from the solution by centrifugation, washed with acidic water (3 times), ethanol (once) and acetone (once) and then dried at room temperature. Neither iron L₃ edge nor iron K edge² indicates Fe^{III} contamination from this samples neither for the NpV (NpL₃ edge²).
- Pu^{IV}/Fe^{II} was obtained by mixing 600 μL of a solution of Pu^{IV} from CEA stock ([Pu]= 1.5 × 10⁻² M; [HNO₃]=1 M) diluted with 400 μL of hydrochloric acid ([HCl]=2 M) to an equimolar solution of K₄[Fe^{II}(CN)]₆ (4.3 mg of K₄[Fe^{II}(CN)]₆ in 1 mL of a 0.2 M HCl solution). The black precipitate was separated from the solution by centrifugation, washed with water (3 times), ethanol and acetone and then dried at room temperature.

Lanthanides samples were prepared following synthesis described in the literature several time following the general aqueous synthesis describe bellow.

2: Methods for P.B.A. characterisation

UV-vis:

Before reaction with ferrocyanides, the actinide redox state in solution solutions were analyzed by UV-vis absorption spectroscopy using a Cary 5000 UV spectrophotometer (Agilent) between 350 and 1100 nm connected to the glovebox cuvette by fiber optics. Powder reflectometry was investigated in a glove box using a Shimadzu UV-2600 spectrophotometer equipped with an integration sphere for reflection measurements. The powder is entrapped between two scotch tape transparent in the visible range. Background removal is performed afterwards using a black scotch tape.

Infrared:

Infrared measurements were performed on the powders using a Bruker Equinox 55 FT-IR spectrometer equipped with an attenuated total reflectance cell. All spectra were collected between 650 and 4000 cm⁻¹ using 32 scans and a resolution of 2 cm⁻¹. The infrared is also a good probe for redox stability of the compounds since both ferricyanide contamination can be assigned using the cyano stretching frequencies at about 2117 cm⁻¹ and Prussian Blue at 2079 cm⁻¹. This is the primary experiment to control samples purity and to avoid reimaging solvent from the powders.

3: S.T.X.M. Measurements

X-ray absorption spectra were obtained at the Molecular Environmental Science Beamline 11.0.2 scanning transmission X-ray microscope (STXM) at the Advanced Light Source (ALS-MES), Lawrence Berkeley National Laboratory, U.S.A.. ³ Soft X-ray STXM is well–suited to the investigation of actinides and radioactive materials, since the amount of material required is very small. It offers the opportunity to investigate radioactive samples in an efficient and safe way. In our experiments, the sample was finely ground in a fume hood dedicated to radiological use and the particles transferred to a 50 nm thick silicon nitride window (1 mm square). A second 50 nm window was glued onto the first and the double window sample package checked to ensure there was no residual contamination. The available energy range was approximately 100 eV–2000 eV and the energy resolution of the measurements was better than 0.1 eV at light element K-edges (C, N, O). The XAS spectrum acquisition was performed by using the STAKS procedure implemented in aXis 2000.⁴

Following this procedure allows to record spectra in several particle areas checking meanwhile the particle homogeneity and redox state in the samples using either the iron L2 and L3 edges and the actinides M4,5 edges as well as lanthanides N4,5 edges. As an example on Figure S.I.1, to check cerium redox state in Ce-PBA, cerium N4,5 edges are used in comparison to tetravalent cerium dioxide in blue.



Figure S.I.1: Comparison of Ce-PBA and cerium dioxide using cerium N4,5 edges

4: EXAFS characterisation of hafnium samples

The hafnium ferrocyanide compound local structure was characterized by Extended X-ray Absorption fine Structure performed at both the iron K edge and the Hafnium L3 edge. The spectra were recorded the soleil synchrotron beamline MARS equipped with a water-cooled Si(111) double crystal horizontal focusing monochromator (DCM). All the measurements were recorded in fluorescence mode using a 13-element high-purity germanium solid-state detector, and were performed at room temperature. Data processing was carried out with the Athena code. After energy calibration, the E0 energy was set at the maximum of the absorption edge. For all samples, this maximum confirmed the redox state + IV for hafnium and +II for iron. The EXAFS signal was extracted by subtracting a linear pre-edge background and a combination of cubic spline functions for atomic absorption background, and then normalizing. These signals were fitted using model clusters derived from the luthetium ferrocyanide crystal structures by use of the Artemis code. Both iron and hafnium EXAFS spectra were fitted together with the same metrical parameter as performed previously for the actinides ferreocyanide structural determination. ^{1, 2}

The k³ EXAFS weighted and corresponding Fourier transformed are presented in the Figure S1. The obtained values for interatomic distances and fit parameters are displayed in table S1.

	dFe-C (Å)	dC-N (Å)	dAn/Hf–O (Å)	dAn/Hf-N(Å)	θ (°)
Hf(IV)/Fe(II) R-factor : 3.35%					
$Amp_{Fe}=0.6$	1.88(1)	1.16(1)	2.15(1)	2.24(1)	169°
ΔE_{0Fe} =-6.8eV	σ ² =0.004Å ²	σ ² =0.004Å ²	σ ² =0.009Å ²	σ ² =0.002Å ²	$\pm 1^{\circ}$
$Amp_{Hf}=0.8$					
$\Delta E_{0Hf} = 7.8 eV$					

Table S1: Fit parameter for the hafnium ferrocyanide



Figure S1: top k³ weighted iron K edge (left) and hafnium L3 edge (right) and corresponding fit (dotted lines). Bottom corresponding Fourier transform magnitude and imaginary par (red) for the iron K edge (left) and hafnium L3 edge (right).

5: Peudo Voight spectra simulation

The pseudo Voight spectra simulation is analogous to the one used in by Dalodiere et al. to reproduce oxygen K edges in plutonium dioxide compounds based on restricted reference lineshapes.⁵ In this case, a sum of a pseudo Voight function (p-V) and step function are applied first to reproduces the K_4 [Fe^{II}(CN)₆] reference spectra by optimizing edge position and p-V maximum energy, amplitude and full width at half maximum (FWHM) using a homemade Excel macro based on the least square optimisation. Then the two primary functions FWHM and energy are restricted to vary in a range of \pm 0.2 eV and two other p-V functions are added to reproduce additional spectral features in An-PBA and Ln-PBA N K edge spectra. The maximum energy, amplitude and FWHM are optimised as floating parameters until the experimental data are reproduces by the sum of the 3 p-V functions and the step functions.

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