EUROPEAN SYNCHROTRON RADIATION FACILITY

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ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

http://193.49.43.2:8080/smis/servlet/UserUtils?start

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

	Experiment title:	Experiment number:
ESRF	Molecular structure of actinide hexcyanometalates	20-01-690

Beamline:	Date of experiment:		Date of report:
BM29	from: 17/04/2010	to: 20/04/2010	10/03/2011
Shifts: 9	**Local contact(s):** C. Hennig		*Received at ESRF:*

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Report:

Among the *quasi* infinity of synthetic molecular edifices, the hexacyanometallate family is well known in transition metal chemistry to behave with remarkable electronic properties. It is also an interesting example of building block chemistry with structurally defined subfamilies. From structure control, electronic delocalization may be tuned up or down in order to design systems that exhibit a large variety of physical properties. This project aims to fully describe the building block chemistry of the actinide cyanometallates and thiocyanometallates and to assess the electronic properties of the actinide-cyano bond using a combination of X-ray spectroscopic and theoretical chemical tools. For the f elements, the lanthanide hexacyanometallate derivatives have been reported extensively, whereas the actinide family is much less present in the literature.

Since the beginning of this project, five series of synthesis have been performed. They have been performed in mid acidic aqueous solution at room temperature, except for the third series in DMF. In most cases, powders have been obtained. Table 1 summarizes the complexes obtained in this task.

Table 1 : list of samples obtained at CEA Marcoule and IPN Orsay. Sample name is designated by the formal oxidation state of the precursors.

Sample name	Final oxidation states	remarks
Series 1		
U^{VI}/Fe^{II}	U^{VI}/Fe^{II}	
U^{VI}/Fe^{III}	$U^{VI}/Fe^{II} + U^{VI}/Fe^{III}$	mixing
Np^{V}/Fe^{III}	Np^{V}/Fe^{III}	
Np^{V}/Fe^{II}	Np^{IV}/Fe^{II}	
Pu^{VI}/Fe^{III}	Pu^{VI}/Fe^{III}	Evolves to Pu^{IV}/Fe^{II} with time
Pu^{VI}/Fe^{II}	Pu^{IV}/Fe^{II}	
Series 2		
Th^{IV}/Fe^{II}	Th^{IV}/Fe^{II}	
U^{IV}/Fe^{II}	U^{IV}/Fe^{II}	
Pu^{IV}/Fe^{II}	Pu^{IV}/Fe^{II}	
Series 3		
$Th^{IV}/Fe^{III}/DMF$	$Th^{IV}/Fe^{III}/DMF$	
$U^{VI}/Fe^{III}/DMF$	$U^{VI}/Fe^{III}/DMF$	
$Np^{IV}/Fe^{III}/DMF$	$Np^{IV}/Fe^{III}+Fe^{II}/DMF$	mixing

$Pu^{IV}/Fe^{III}/DMF$	$Pu^{IV}/Fe^{III}/DMF$	
Series 4		
Am^{III}/Fe^{III}	Am^{III}/Fe^{III}	Becomes Am^{III}/Fe^{II} with time
Am^{III}/Fe^{II}	Am^{III}/Fe^{II}	
Cf^{III}/Fe^{II}	Cf^{III}/Fe^{II}	
Series 5		
Lu^{III}/SCN	Lu^{III}/SCN	

We have already reported on the results of series 4 (report of the 06/07/2010) with the Am and Cf adducts. We would like to report here on series 3. For EXAFS data analysis, an original parameterized fitting procedure based on the two edge fit has been implemented and tested on model compound **$Lu^{III}/Fe^{III}/DMF$** ($[Lu^{III}(DMF)_4(H_2O)_3(Fe^{III}(CN)_6)].H_2O$) described by Mullica.[1] The model compound **$Lu^{III}/Fe^{III}/DMF$** ($[Lu^{III}(DMF)_4(H_2O)_3(Fe^{III}(CN)_6)].H_2O$) has been selected to test the parameterized fitting procedure. In this complex, the lutetium atom is eight-coordinated to four DMF groups, three water molecules and only one ferricyanide motif. It contains one "Fe-C-N-Lu" link, therefore of very weak intensity. In order to test our fitting procedure, both iron K edge and Lu L_{III} edge of **$Lu^{III}/Fe^{III}/DMF$** have been adjusted using a parameterization of the metrical parameters at both edges. In the crystal structure of **$Lu^{III}/Fe^{III}/DMF$**, the Fe-C-N angle is equal to 177 ° and can be considered nearly linear while the Lu-N-C angle (noted θ) is equal to 164°. Similarly, the Th(IV) adduct $(H_5O_2)[Th(IV)(DMF)_5(H_2O)]_2 [Fe(III)(CN)_6]_3$ as well as Np(IV) and Pu(IV) adducts (but not crystallized) have been prepared. As confirmed by XANES measurements (at both actinide and Fe edges) they show (except for the Np adduct, as detailed in Table 1) an interesting stability of the An^{IV}/Fe^{III} form instead of An^{IV}/Fe^{II} form in the absence of DMF. Figure 1 exemplifies the two edge fitting methodology from the **$Lu^{III}/Fe^{III}/DMF$** model compound.
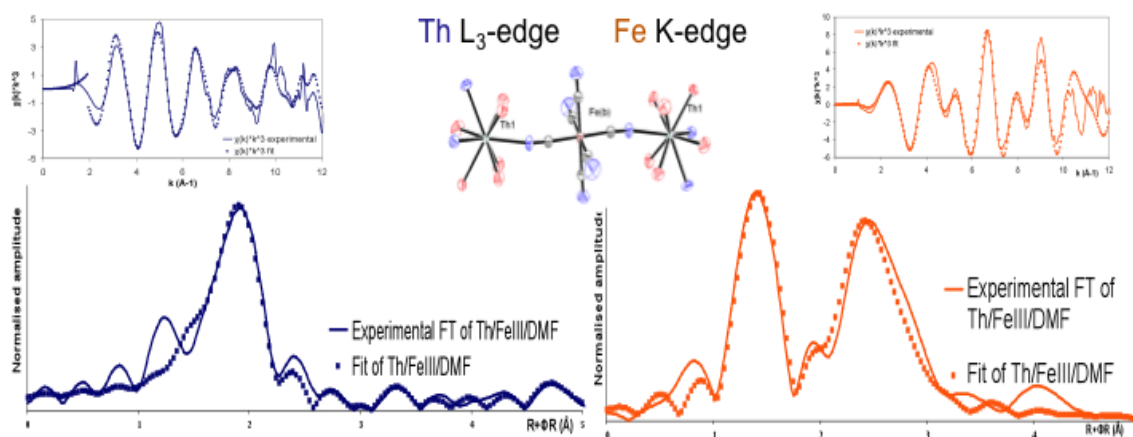

Fig. 1 : two edge fitting procedure of $(H_5O_2)[Th(IV)(DMF)_5(H_2O)]_2$ [Fe(III)(CN)$_6$]$_3$. The Fe K edge was recorded at the SSRL synchrotron.

The best fit metrical parameters of **$Th^{IV}/Fe^{III}/DMF$** are in very good agreement with the crystallographic data. EXAFS data : Th-N = 2.59 Å (σ^2=0.006 Å), C-N = 1.17 Å (σ^2=0.010 Å), Fe-C = 1.92 Å (σ^2=0.009 Å) ; XRD data : Th-N = 2.578 Å, C-N = 1.149 Å, Fe-C = 1.923 Å. We are currently working on the adjustment of the **$Pu^{IV}/Fe^{III}/DMF$** adduct. One of the objectives is to understand the role of the DMF in the structure in preventing the formation of the ferrocyanide adduct.

In parallel, we have started the investigation of the actinide thiocyanide adducts. Crystallographic parameters have already been obtained from lanthanide (Nd and Lu) and thorium $[NBu_3]_3[Th(NCS)_4(NO_3)_3]$ adducts. A first attempt in the synthesis of the Am(III) thiocyanate equivalent has failed and will be the object of the next beam time period.

1 D. F. Mullica, J. M. Farmer, B. P. Cunningham, J. A. Kautz, *J. Coord. Chem.*, **49**, 239 (2000).