



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: Molecular structure of actinide hexacyanometalates	Experiment number: 20-01-190
Beamline: BM29	Date of experiment: from: 02/10/2009 to: 05/10/2009	Date of report: 06/07/2010
Shifts: 9	Local contact(s): C. Hennig	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Christophe DEN AUWER* ^a DEN/DRCP/SCPS G. Dupouy* DEN/DRCP/SCPS T. Dumas* DEN/DRCP/SCPS a CEA Marcoule 30207 Bagnols sur Cèze, France		

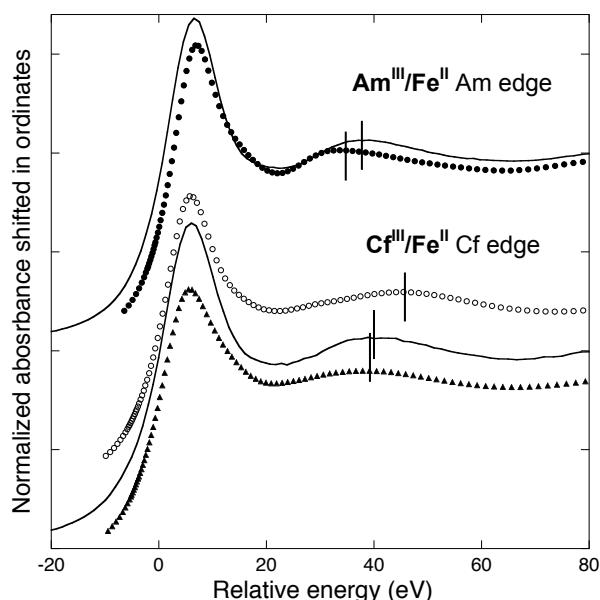
Report:

Among the *quasi* infinity of synthetic molecular edifices, the hexacyanometallate family is well known in transition metal chemistry to foster remarkable electronic delocalization along the metal-cyano-metal bond. Furthermore, this delocalization may be tuned up or down in order to design systems that exhibit a large variety of physical properties. From a structural point of view, the $\text{KLn}^{\text{III}}/\text{Fe}^{\text{II}}(\text{CN})_6 \cdot x\text{H}_2\text{O}$ (Ln = lanthanide element) family can be separated in three series. The first one with $\text{Ln} = \text{La}$ to Nd presents the general formula $\text{KLnFe}^{\text{II}}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ [1]. These compounds crystallize in the hexagonal $\text{P6}_3/\text{m}$ space group. The second series has a unique representative, $\text{KSmFe}^{\text{II}}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$, which crystallizes in a monoclinic group ($\text{P2}_1/\text{m}$) [2]. For these two series, the nine-coordinated lanthanide cation is bound to six $\{\text{Fe}(\text{CN})_6\}$ motifs and to three water molecules in a distorted trigonal tricapped prism. Finally the third series involves $\text{Ln} = \text{Eu}$ to Lu . They all occur in the orthorhombic space group: $\text{KLnFe}^{\text{II}}(\text{CN})_6 \cdot 3.5\text{H}_2\text{O}$ crystallizes in the Cmcm space group [3] while $\text{KLnFe}^{\text{II}}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ crystallizes in the Pnma space group [4]. The difference between the two space groups is the lanthanide coordination number: in the Cmcm group the lanthanide cation is nine-coordinated like for the La-Nd series; in the Pnma group the lanthanide cation is eight-coordinated to six nitrogen atoms and only two water molecules.

A few years ago we have started describing the molecular and electronic structures of the materials formed by the $\{\text{Fe}(\text{CN})_6\}$ building blocks and actinide(IV) ($\text{An} = \text{Th}, \text{U}, \text{Np}$). We have compared these new materials to their homologues of the lanthanide series, our major interest originated in fundamental understanding of actinide *versus* lanthanide chemistry. In this report we present briefly the first investigation of americium and californium hexacyanoferrates, two actinide cations from the middle of the actinide series. Americium is considered as the first element of the series with stronger lanthanide character (Americium is often considered as a turning point in actinide chemical properties) and californium is the heaviest element available in the laboratory for weighable chemistry. Both elements are also very good representatives of the +III actinide chemistry with no other stable oxidation state achievable in our experimental conditions.

Figure 1 shows the experimental XANES spectrum at the Cf and Am L_3 edge of $\text{Am}^{\text{III}}/\text{Fe}^{\text{II}}$ and $\text{Cf}^{\text{III}}/\text{Fe}^{\text{II}}$ respectively. The absorption edges have all been rescaled with respect to the edge ramp for comparison. As expected, the Am and Cf L_3 edges are very similar since both cations are at the same oxidation state in similar environments. In addition, in order to fully characterize the actinide coordination sphere, the EXAFS spectra of $\text{Am}^{\text{III}}/\text{Fe}^{\text{II}}$ and $\text{Cf}^{\text{III}}/\text{Fe}^{\text{II}}$ at the actinide L_{III} edge have also been recorded and adjusted [5].

In the following discussion we detail the comparison between $\text{Am}^{\text{III}}/\text{Fe}^{\text{II}}$ with the neodymium equivalent on the one hand, and $\text{Cf}^{\text{III}}/\text{Fe}^{\text{II}}$ with the gadolinium equivalent on the other hand.



Experimental XANES spectra at the Am L₃ edge of **Am^{III}/Fe^{II}** and at the Cf L₃ edge of **Cf^{III}/Fe^{II}** (straight line). Comparison with the simulated spectra (Feff84) of KNdFe^{II}(CN)₆.4H₂O^[7d] (black dots), KGdFe^{II}(CN)₆.3H₂O^[10b] (black triangles) and KGdFe^{II}(CN)₆.3.5H₂O^[9b] (white dots). Spectra have all been shifted in energy with respect to absorption ramp.

In KNd^{III}Fe^{II}(CN)₆.4H₂O, the neodymium cation is nine coordinated to six nitrogen atoms ($d(\text{NdN}) = 2.52 \text{ \AA}$) and three water molecules ($d(\text{NdO}) = 2.68 \text{ \AA}$). A direct comparison between the distances obtained by EXAFS for **Am^{III}/Fe^{II}** (not shown, see [5] for details) and the above ones suggests that the americium and neodymium environments are analogous. Therefore, by analogy, **Am^{III}/Fe^{II}** must contain nine-coordinated {AmN₆(H₂O)₃} units. Consequently, as shown in Figure 1 by comparing the experimental and simulated (from KNdFe^{II}(CN)₆.3H₂O) XANES spectra, the americium polyhedron may be attributed to a tri-capped trigonal prism in which the americium is bonded to six nitrogen atoms in apical sites and to three water molecules in the equatorial plane. Simulations have been performed here by replacement of the lanthanide atomic number in the input file by the corresponding actinide number (*i.e.* Nd replaced by Am), everything else being kept equal to the crystal structure.

Comparison between the californium ionic radius and the gadolinium one suggests that **Cf^{III}/Fe^{II}** may crystallize as KGdFe^{II}(CN)₆.3.5H₂O or as KGdFe^{II}(CN)₆.3H₂O do. As described in the introduction, gadolinium adducts may occur in two different forms: KGdFe^{II}(CN)₆.3.5H₂O crystallizes in an orthorhombic space group (Cmcm) with a coordination number of nine, while KGdFe^{II}(CN)₆.3H₂O crystallizes in a orthorhombic space group (Pnma) with a coordination number of eight. Figure 1 compares the experimental XANES spectra of **Cf^{III}/Fe^{II}** at the Cf L₃ edge to two simulations carried out from the gadolinium analogues : KGdFe^{II}(CN)₆.3H₂O and KGdFe^{II}(CN)₆.3.5H₂O. Although the direct comparison must be taken with care, it appears clearly that in the case of **Cf^{III}/Fe^{II}**, the position of the first oscillation (vertical mark in Figure 1) is in better agreement with that of simulated KCf(Gd)Fe^{II}(CN)₆.3H₂O than with that of simulated KCf(Gd)Fe^{II}(CN)₆.3.5H₂O. In conclusion, all the above results strongly suggest that **Cf^{III}/Fe^{II}** may be written as KCf^{III}Fe^{II}(CN)₆.nH₂O as in KGdFe^{II}(CN)₆.3H₂O. This has been also confirmed by the EXAFS data analysis (not shown, see [5] for details).

The striking point of this study is the decrease of coordination number by one unit going from neodymium (americium) to gadolinium (californium), from trigonal tricapped prism for the first ones to trigonal bicapped prism for the second ones. This example is to be related to the latest studies on the aquo or hydrate adducts for the lanthanide and the actinide series at oxidation state +III [6].

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