



## Application for beam time at ESRF – Experimental Method

Template for ESRF Standard proposals, CRG proposals, MX Rolling Crystallography and MX Rolling BioSAXS proposals.

This document should consist of a **maximum** of **two A4 pages** (including references) with a minimal font size of **12 pt**.

### **Proposal Summary (should state the aims and scientific basis of the proposal):**

The goal of our research in the long term is to improve our understanding of the fundamental chemistry of the actinides and their bond properties. Our approach is to systematically compare series of molecular metal-organic complexes. In a first step, inactive actinide homologues are envisaged for establishing a strategy for measurement and data analysis of such compounds. To this end, we require high-resolution molecular structures and also their electron density maps, which can only be derived from HR-SC-XRD experiments. Our research can benefit from such synchrotron-based SC-XRD, as this type of experiment not only allows a structure determination on an atomic level, but is even suitable for detecting the electronic structure in form of an electron density distribution in a high-resolution measurement mode.

### **Scientific background:**

The actinides are a group of radioactive heavy elements with a high relevance due to their application in nuclear power generation and the challenges associated with the safe long-term disposal of nuclear wastes.<sup>1</sup> Yet, the handling of particularly the transuranium elements Np, Pu, and Am is limited to select facilities with the appropriate laboratories and licenses, which severely limits our knowledge of even basic chemical properties of these elements.<sup>2</sup> Their complex redox chemistry with accessible oxidation states between +II and +VII, where often multiple oxidation states can be present simultaneously, adds to the difficulties in these experiments. One major scientific question concerns the participation of the actinides' *5f* electrons in bonding, as opposed to the inertness of the lanthanides' *4f* electrons.<sup>3</sup>

Our approach to address this question is the synthesis and characterization of isostructural series of actinide compounds with increasing number of *f*-electrons and analogue compounds of transition metals and lanthanides. We characterize the solid state structures of these compounds by single crystal-XRD and IR spectroscopy and the complex speciation by NMR and UV/vis spectroscopy.<sup>4-6</sup> Based on this structural characterization, quantum chemical calculations can then be applied to analyse the bonding situation in these compounds in detail. This requires high-level relativistic calculations, thus a detailed characterisation in advance is essential for meaningful calculations.<sup>4-8</sup>

Here high-resolution X-ray diffraction and the extraction of electron density maps can provide a hitherto unknown level of precision in the experimental localisation of electron density between the atoms, in particular between the metal centre and coordinating ligand donor atoms. They can yield valuable insight into the bond properties of actinides in comparison with transition metals or lanthanides as resolutions of HR-SC-XRD exceeds those of standard lab diffractometers significantly, and could simultaneously help determining the oxidation state of the metal centres.

### **Experimental technique(s), required set-up(s), measurement strategy, sample details (quantity...etc):**

We plan high-resolution single-crystal diffraction (HR-SC-XRD) measurements at 100 K for determination of electron distribution, and the extraction of electron density maps at ROBL.

First, we will test the experimental possibilities of XRD-2 with insensitive as well as inactive samples, also in comparison to standard SC-XRD measurements previously performed at HZDR. The tests of HR-SC-XRD include the selection of crystals of high quality and appropriate size, as well as finding a suitable combination of measurement parameters like X-ray energy, exposure time, slicing, etc. A whole series of complexes with systematically changing tetravalent transition metal centre will be used for this first part. Here, the focus is on growing complexity of the electronic structure of the metal centre (*3d*, *4d*, *5d*), being of significant importance for data analysis of electron density maps. In addition, such a series can further allow a comparison between tetravalent transition metals and tetravalent actinides. Our experiments are aimed to serve as preliminary tests for highly radioactive actinide compounds, also including transuranic elements as a feasibility study. For those, the combination of experiments and technique with the samples

can only be carried out at BM-20 at the ESRF, in particular as none of the other beamlines is capable to handle transuranic elements, which are the focus of our work in a long-term perspective.

Secondly, we plan to take the step to more sensitive inactive lanthanide complex samples after implementing the measurement routine. This will open up the possibility for future HR-SC-XRD measurements and electron density map generation of radioactive and oxygen/moisture sensitive actinide samples, and it will furthermore allow a direct comparison of the electronic structure of lanthanide (4f) vs. actinide (5f) coordination.

Crystalline samples for measurement will be synthesized and isolated at HZDR in advance. It is planned to prepare two series of samples for measurement, as those samples were already found to yield large and well-diffracting single crystals, suitable for high-resolution measurements:

- 1) HR-SC-XRD measurements of  $[M^{IV}(\text{PyO})_4]$  complexes with  $M^{IV} = \text{Ti, Zr, Hf}$
- 2) HR-SC-XRD measurements of  $[\text{Ln}^{III}(\text{Lig})_3]$  complexes with  $\text{Ln}^{III} = \text{La, Eu, Yb}$  as well as  $[\text{Ce}^{IV}\text{Cl}(\text{Lig})]$

### **Beamline(s) and beam time requested with justification:**

In this proposal are foreseen only inactive compounds. The experiment will be performed on the XRD-2 diffractometer with either the Huber kappa or the ARINAX goniometer. The excitation energy will be fixed at 22 keV.

We request a total measurement time of four days. This includes one day for diffractometer alignment and detector calibration. The number of samples as outlined above cannot be measured in less time with sufficient quality. We calculate 4 hours for preliminary tests, as well as 2 hours per sample. When analyzing these experiments additional time must be allotted for changes in the measurement setup, especially when recognizing X-ray synchrotron radiation damages with increasing structural resolution.

### **Results expected and their significance in the respective field of research:**

The expected results will improve the general understanding of opportunities and restrictions of the high-resolution SC-XRD methods like electron density map generation for heavy atom structures. Currently, there are only a few publications providing electron density maps of heavy atom structure. As such, the results of these measurements will be the basis for establishing a new and powerful method for actinide bond characterization, in particular in combination with quantum chemical calculations (QCC) as well as HERFD-XANES data. We expect to obtain structural and electronic information on molecular transition metal- and lanthanide compounds of a hitherto unknown level of precision with hard (*O*) and medium donors (*N*) of different sensitivity, electronic complexity, and oxidation state. Such data will provide an experimental insight into electron density parameters that are currently only accessible via QCC by doing a QTAIM (quantum theory of atoms in molecules) analysis, and extraction of yielded delocalization indices. The research laid-out here, involves three postdocs and two PhD students, and will contribute to their theses. In addition, the results are expected to contribute to a number of publications in peer-reviewed journals.

### **References**

- [1] H. Geckeis, *et al.*, *Chem. Rev.*, **113**, 1016 (2013).
- [2] P. D'Angelo, *et al.*, *Inorg. Chem.*, **52**, 10318 (2013); B. Drobot, *et al.*, *Chemical Science*, **6**, 964 (2015).
- [3] G. R. Choppin, *et al.*, in *The Chemistry of the Actinide and Transactinide Elements, Vol. 4*, 4th ed., Springer, **2011**.
- [4] T. Radoske, J. März, M. Patzschke, P. Kaden, O. Walter, M. Schmidt, T. Stumpf, *Chem. Eur. J.* **2020**, *26*, 16853-16859.
- [5] S. Fichter, S. Kaufmann, P. Kaden, T. S. Brunner, T. Stumpf, P. W. Roesky, J. März, *Chem. Eur. J.* **2020**, *26*, 8867-8870.
- [6] T. Radoske, R. Kloditz, S. Fichter, J. März, P. Kaden, M. Patzschke, M. Schmidt, T. Stumpf, O. Walter, A. Ikeda-Ohno, *Dalton Trans.* **2020**, *49*, 17559-17570.
- [7] R. Kloditz, S. Fichter, S. Kaufmann, T. S. Brunner, P. Kaden, M. Patzschke, T. Stumpf, P. W. Roesky, M. Schmidt, J. März, *Inorg. Chem.* **2020**, *59*, 15670-15680.
- [8] L. Köhler, M. Patzschke, M. Schmidt, T. Stumpf, J. März, *Chem. Eur. J.* **2021**, *27*, 18058-18065.