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 via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can 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.

ESRF	**Experiment title:** Electronic Structure of Osmium Complexes as Analogues of Ruthenium Anticancer Drugs	**Experiment number**: LS-3005
Beamline: ID18	**Date of experiment**: from: July 13 to: July 19 2021	**Date of report**: 18/01/2022
Shifts: 18	**Local contact(s)**: Dr. Dimitrios Bessas (email: dimitrios.bessas@esrf.fr)	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

In the allocated beamtime we measured the nuclear forward spectra of the following series of ^{187}Os-enriched complexes in oxidation states +6, +5, +4, and +3:

$K_2[Os^{VI}O_2(OH)_4]$ (**1**)

$[Os^{V}Cl_6](C_{24}H_{20}P)$ (**2**)

$[Os^{IV}Cl_5(C_7H_6N_2)](C_7H_7N_2)$ fr_2 brown, 1*H*-ind (**3**) with (**4**) as minor species in ratio 7.6:1

$[Os^{IV}Cl_5(C_7H_6N_2)](C_7H_7N_2)$ fr_1 violet, 2*H*-ind (**4**)

cis-$[Os^{IV}Cl_4(C_7H_6N_2)_2]$ (**5**)

$[Os^{IV}Cl_6](C_3H_5N_2)_2$ (**6**)

$[Os^{IV}Cl_6](C_{24}H_{20}P)_2$ (**7**)

mer-$Os^{III}Cl_3(C_3H_4N_2)_3$ (**8**)

trans-$Os^{III}Cl_2(C_3H_4N_2)_4]Cl$ (**9**)

The measurements were performed at ID18/ESRF using a high resolution monochromator with instrumental resolution of 0.5 meV. The data acquisition procedure was smooth and the quality of the obtained data was excellent. The nuclear forward scattering (NFS) of complexes **1**–**9** were different in accord with their different coordination environment and symmetry. In addition, nuclear inelastic scattering (NIS) spectra of complexes **1**, **4**, **5**, and **9** were measured. The raw NFS spectra for compounds **1** and **9** are presented in Figure 1, while NIS spectra are shown in Figure 2.

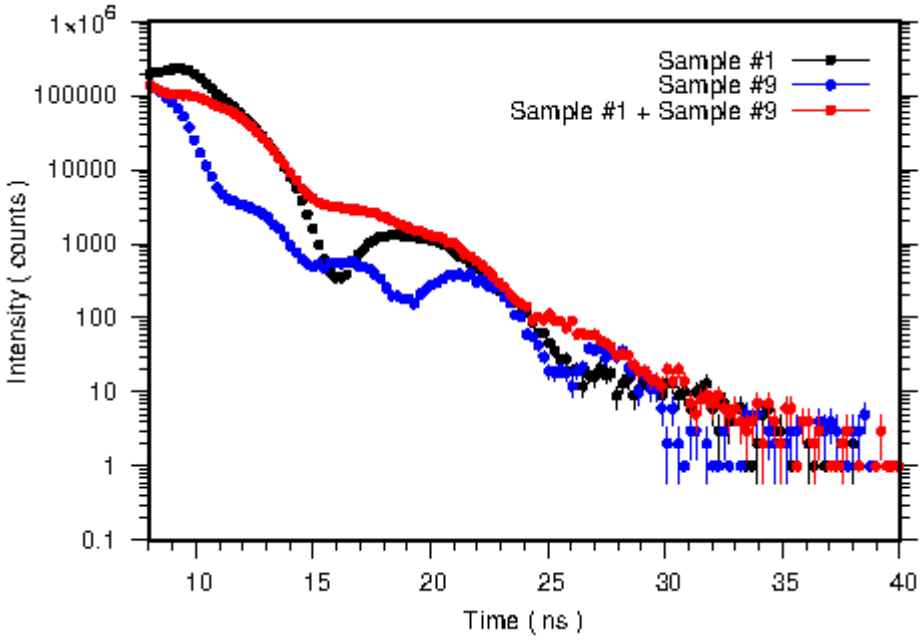

Figure 1. NFS spectra for compounds **1** and **9** measured separately and together with the beam oriented perpendicular to the sample.

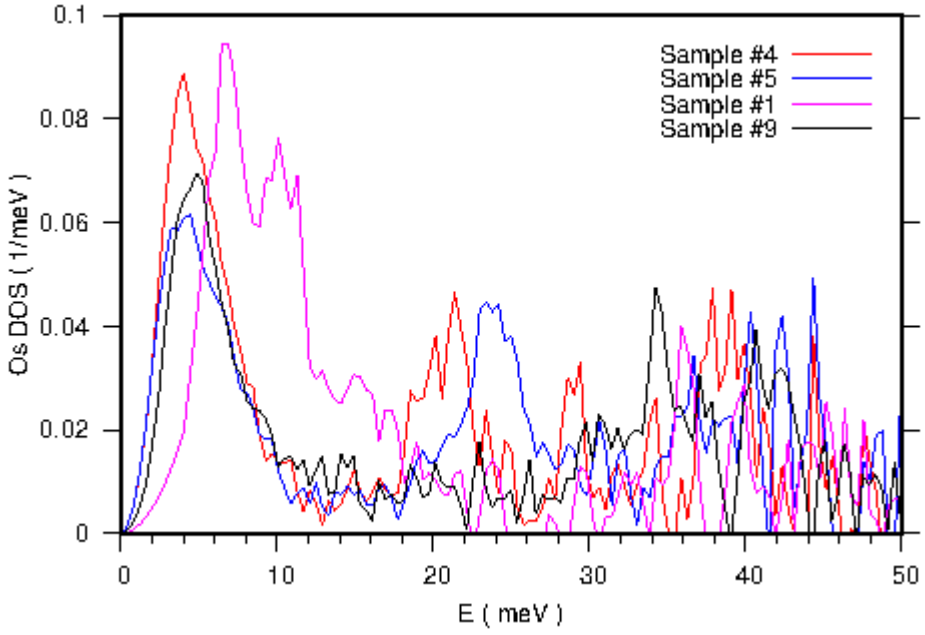

Figure 2. NIS spectra of compounds **1**, **4**, **5**, and **9**.

The performed measurements allowed for obtaining benchmarking information with regard to co-relation of the Os oxidation state with isomer shift (I.S.) in Mössbauer spectra and on the local coordination (the so-

called quadrupole splitting ΔE_Q), as well as on the vibrational properties (summarised in the density of vibrational states of Os) for complexes **1**, **4**, **5**, and **9** (from nine available).
For all these compounds, the isomer shifts (I.S.) and quadrupole splitting parameters (ΔE_Q) were extracted by fitting the experimental NFS spectra measured vs time (Figure 1). A model was developed with which both nuclear forward spectra and Mössbauer data were fitted simultaneously.

The allocated beamtime was not enough to perform the measurements for osmium compounds in oxidation states +8 and +2 (which are crucial as these are the two extrema among the systems of interest), as well as to carry out measurements at lHe temperature. The NIS spectra were measured for four from nine available compounds, since these are time-consuming measurements. Under such circumstances it seems imperative to request additional beamtime.