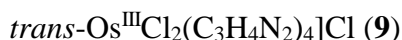
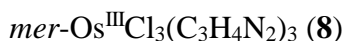
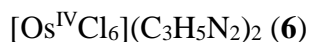
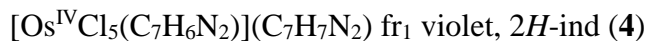
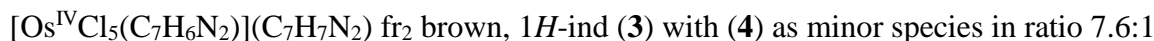
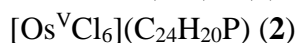
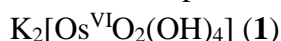




	Experiment title: Electronic Structure of Osmium Complexes as Analogues of Ruthenium Anticancer Drugs	Experiment number: LS-3162
Beamline: ID18	Date of experiment: from: September 6 to: September 12, 2022	Date of report: 08/09/2023
Shifts: 18	Local contact(s): Dr. Dimitrios Bessas (email: dimitrios.bessas@esrf.fr)	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): V. Arion ^{1,*} , G. Büchel ^{1,*} , G. Cutsail ^{2,*} , S. DeBeer ² , J. Telser ³ , S. Komorovský ⁴ ¹ Universität Wien, Institut für Anorganische Chemie, 1090 Wien, Austria ² MPI for Chemical Energy Conversion, 45470 Mülheim an der Ruhr, Germany ³ Roosevelt University, Biological, Physical and Health Sciences, Chicago, IL 60605 USA ⁴ Slovak Academy of Sciences, Institute of Inorganic Chemistry, SK-84536 Bratislava, Slovakia		

Report:

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



The measurements were performed at ID18/ESRF using a high-resolution monochromator with instrumental resolution of 1.05 meV. The data acquisition procedure was smooth and the quality of the obtained data was excellent. The nuclear forward scattering (NFS; see Fig. 1) of complexes **1–9** were different in accord with their different coordination environment and symmetry. In addition, nuclear inelastic scattering (NIS; see Fig. 2) spectra of all nine complexes were measured.

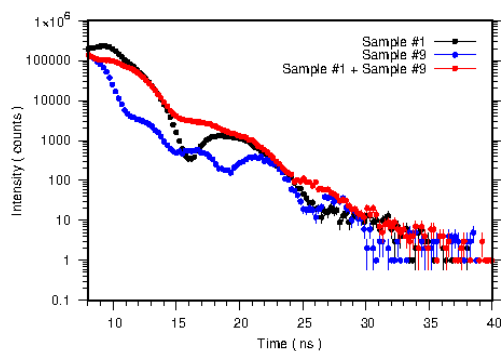


Figure 1. NFS spectra for compounds **1** and **9** measured separately and together with the beam oriented perpendicular to the sample.

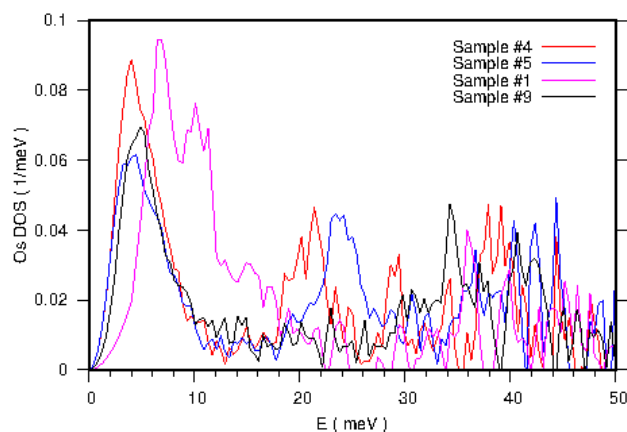


Figure 2. NIS spectra of compounds **1**, **4**, **5**, and **9**.

The performed measurements allowed for obtaining benchmarking information with regard to 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 nine complexes (from 11 available). For these nine compounds, the ΔE_Q were extracted by fitting the experimental NFS spectra measured vs time as shown in Figure 3 for one of the compounds measured. A model was developed in which both NFS and Mössbauer data were fitted simultaneously.

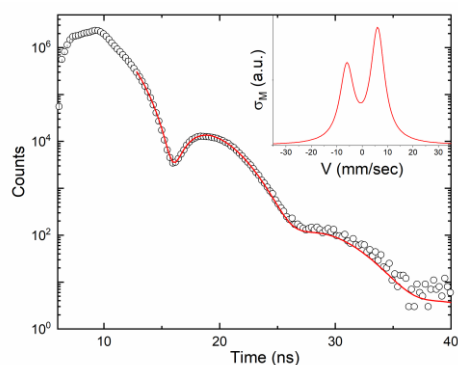


Figure 3. ^{187}Os NFS time spectrum measured at room temperature on $\text{K}_2[^{187}\text{OsO}_2(\text{OH})_4]$ with fit (red trace). Inset: simulation of the Mössbauer cross-section versus Doppler drive velocity.

The allocated beamtime was not enough to perform the measurements for osmium(VI) compounds $\text{Et}_4\text{N}[\text{Os}^{\text{VI}}\text{Cl}_4(\text{N})(\text{H}_2\text{O})]$ and $n\text{Bu}_4\text{N}[\text{Os}^{\text{VI}}\text{Cl}_4(\text{N})]$, as well as to carry out additional measurements, which would allow for extraction of isomer shift (I.S.) data at 300 K. Under such circumstances it seems imperative to request additional beamline time.