



	Experiment title: Au L-edge XAS of gold complexes: one-electron processes @ gold	Experiment number: CH-5954
Beamline: BM23	Date of experiment: from: 02/08/2021 to: 05/08/2021	Date of report: 13/09/2021
Shifts: 9	Local contact(s): Cesare Atzori	<i>Received at ESRF:</i>

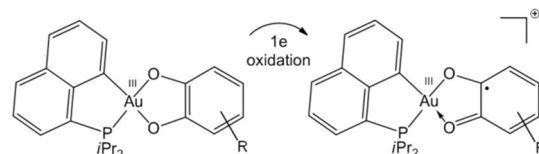
Names and affiliations of applicants (* indicates experimentalists):

Vlad Martin-Diaconescu - (ALBA Synchrotron, Cerdanyola del Valles, Spain)

SZALOKI Gyorgy (Université Paul Sabatier: Toulouse, Midi-Pyrénées, France)

Report

There is significant interest in Au based complexes as potential redox switchable catalysts with reversible on-demand control of catalytic activity, as well as applications in photoredox catalysis. Although, significant progress has been made in Au chemistry, the focus has largely been on Au(I) and Au(III) complexes. Au(IV) complexes are unprecedented and single-electron processes are extremely rare. Therefore we have begun a comprehensive study to explore Au(III) complexes featuring redox active ligands (fake Au(IV) complexes) with the aim to open a new facet in gold chemistry. Herein, we applied Au L-edge spectroscopy as a direct probe of oxidation state and coordination environment at the Au center. A family of Au(III)-catechol based and analogous complexes were characterized and changes upon one electron oxidation investigated.

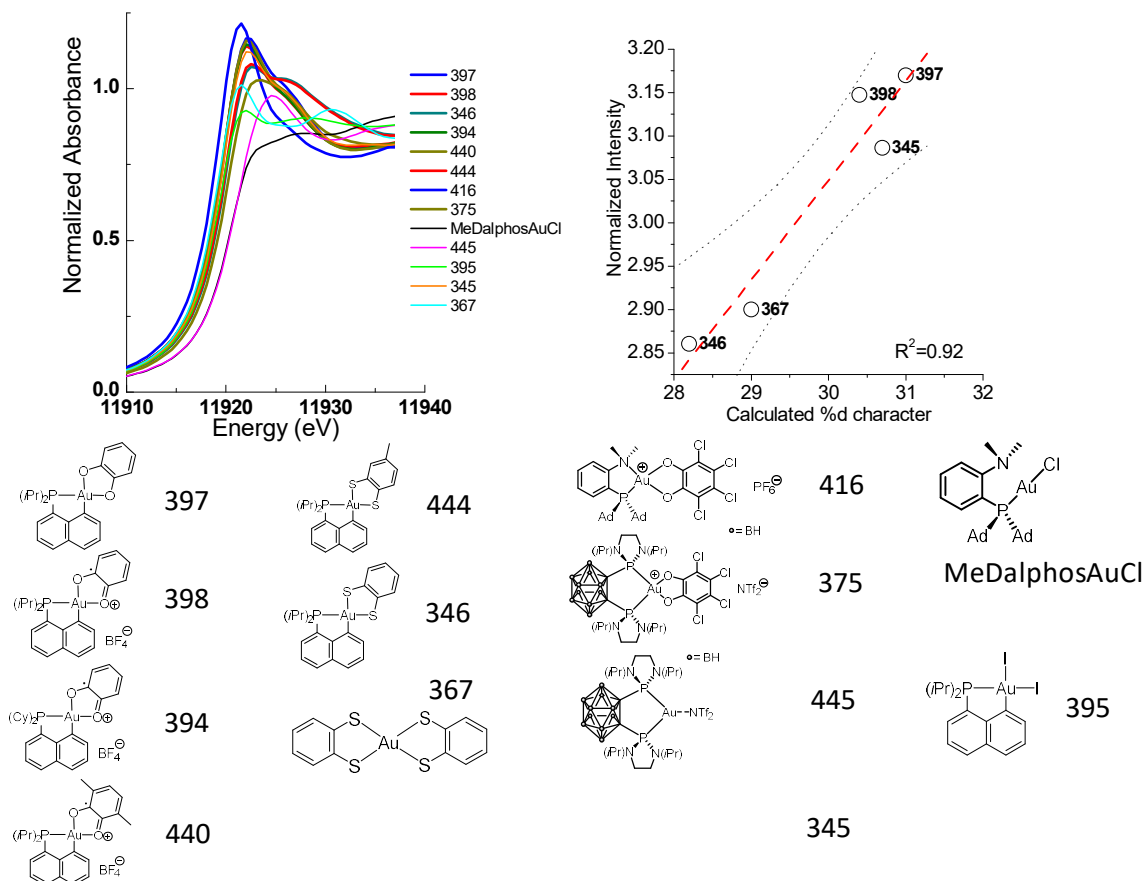


Transmission data were collected on pellets diluted in cellulose at cryogenic temperature (20K) using a helium cryostat. Our main goal is to characterize the one electron oxidation of Au(III) complexes featuring redox active ligands. This requires correlation of theoretical models with experimental data of the electronic structure of the complexes in their reduced and oxidized form. Therefore Au L-edge spectroscopy was applied in order to:

1. Build a spectra library of Au complexes having redox active ligands as standards for calibration of theoretical calculations;
2. Observe the changes upon one electron oxidation of Au(III)-catechols, determine the locus of oxidation and if Au-Au stacking interactions occur upon oxidation.

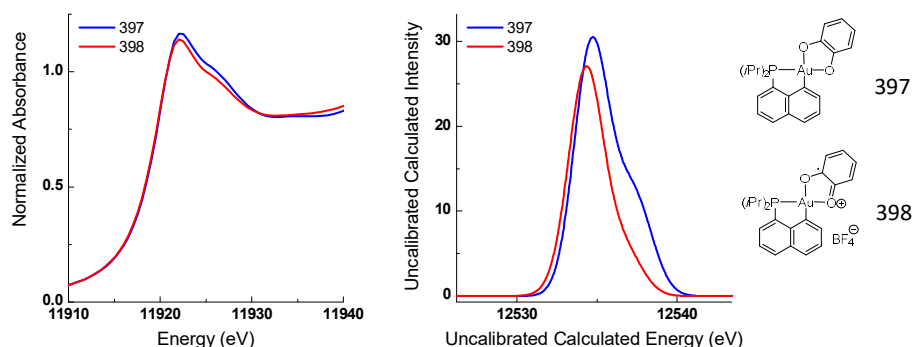
1. Build a spectra library of Au complexes having redox active ligands as standards for calibration of theoretical calculations.

Data on a concrete series of complexes having a variety of ligands and ligand substituents including the previously explored Au(III)bis(dithiobenzene) were collected to serve as the experimental benchmark for our theoretical calculations. These complexes not only serve as reference compounds but potential species for one electron oxidation. As previously reported the area of metal L-edge XANES features correlate to oxidation state and the amount of percent metal d-character. Our preliminary (BP86/def2-TZVP) ground state calculations correlate well with the experimental data suggesting the level of theory employed in our models is adequate.

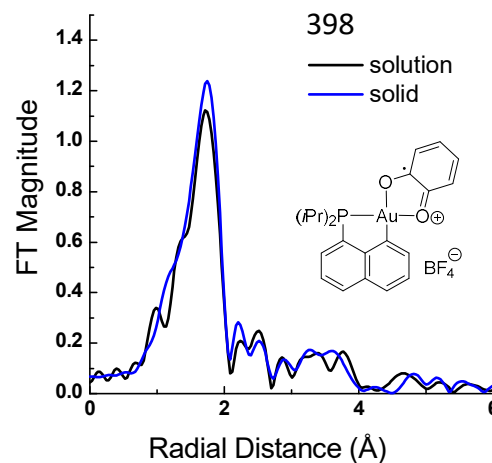


2. Observe the changes upon one electron oxidation of Au(III)-catechols, determine the locus of oxidation and if Au-Au stacking interactions occur upon oxidation.

Transmission data for the reduced 397 and oxidized 398 form show marked differences in the XANES region as predicted by theory. A drop in intensity in the whiteline occurs as the percent of d character in the empty Au d-manifold drops. This is somewhat counter intuitive as the Au-catechol interaction is expected to become weaker and less covalent which should result in a more localized Au d-manifold leading to a more intense signal at the Au L3-edge upon oxidation. We hypothesize that the bonding trans phosphine ligand is compensating. This is currently under investigation. However, it is clear that the oxidation state of +3 at the Au center does not change upon one electron oxidation of the complex.



Lastly, complementary data point to the possible existence of intermolecular interactions in the solid state upon one electron oxidation of 397 yielding 398. Therefore, we questioned whether Au-Au interactions are detectable. EXAFS data collected in solution and solid state indicate that this is not the case. If intermolecular interactions exist, these are most probably the ordering π - π stacking of the ligands which are expected to occur at 3.5 Å.



Publications:

At least three publications are currently envisioned focusing on three main points:

1. A calibration study for spectral calculation using TDDFT (no spin orbit coupling employed taking advantage of the weak coupling interaction between 2p and 5d orbitals) as well as restricted open shell configuration interaction with singles - ROCIS (spin orbit coupling employed) approaches at the Au L-edge. This will serve as a benchmark study for the field.
2. Characterization of one electron oxidation of Au(III)-catechols using Au L-edge and complementary spectroscopic techniques followed by correlation to theory.
3. Characterization of one electron oxidation of S[^]S analogues (benzene dithiolate) of Au(III)-catechols from both the metal and ligand perspective using Au L-edge and S K-edge spectroscopy (*additional data at both edges is still required*).