ESRF	**Experiment title:** Circularly polarised X-ray excited optical luminescence (CP-XEOL) study of lanthanides molecular magnets	**Experiment number**: CH-7153
Beamline: ID12	**Date of experiment**: from: 05.02.2025 to: 11.02.2025	**Date of report**: 09.05.2025
Shifts: 18	**Local contact(s)**: Dr Andrei Rogalev	*Received at ESRF:*

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Report:

The aim of experiment CH-7153 was to measure (magnetic) circularly polarised X-ray excited optical luminescence (CP-XEOL and MCP-XEOL) of our compounds in hard X-rays in solution and in the solid state. These measurements would become a key reference for future CP-XEOL and MCP-XEOL investigations. Unfortunately the XEOL setup was not operational. We have managed to check the resistance of the samples to hard X-ray irradiation. No radiation damage was observed in these samples. Due to above difficulties, the beamtime was used for XANES measurements on the samples.

The series of XANES spectra at room temperature were measured for three types of samples: chlorine based (Cl K-edge), bromine based (Br K-edge) and iodine based (I L_1-edge). The main aim was to see if there are any distinguishing features between the spectra depending on the type of bond formed by the halogen atom in different model compounds, and what these features are. For each halogen, three model compounds were chosen:

- for the covalent bond: C_6Cl_6, C_6Br_6 and C_6I_6,
- for the coordination bond: $CoCl_2$, $CoBr_2$ and CoI_2,
- for the ionic bond: NaCl, NaBr and NaI.

Using these spectra as a reference, we were able to analyse the nature of the bonds formed by the halogens in the new compounds synthesised in our laboratory: C_6O_6@2Cl, C_6O_6@2Br and C_6O_6@2I, in which the neutral C_6O_6 ring is "sandwiched" between two halogen atoms at an unprecedentedly close distance. Comparisons of the measured XANES spectra are presented in Figures 1-3 for Cl K-edge, Br K-edge and I L_1-edge, respectively.

Many different sample preparation methods were tested during beamtime to avoid diffraction peaks in the XANES spectra. All samples were measured as finely ground powder in paraffin oil, as finely ground powder in NVH immersion oil and as solutions in various solvents depending on solubility (e.g. acetonitrile, *N*-methyl-2-pyrrolidone). Samples in the form of solutions were measured both directly in cube holders and in sealed glass capillaries glued to the cube holder. For both types of liquid sample packing, the solvent evaporation was the main problem. We checked the state of each sample after measurement - most were found to be measured as a thin layer of crystalline solid. We also measured XANES spectra for paraffin oil, NVH immersion oil and Kapton tape (used to cover the samples) to check for the presence of Cl, Br and I.

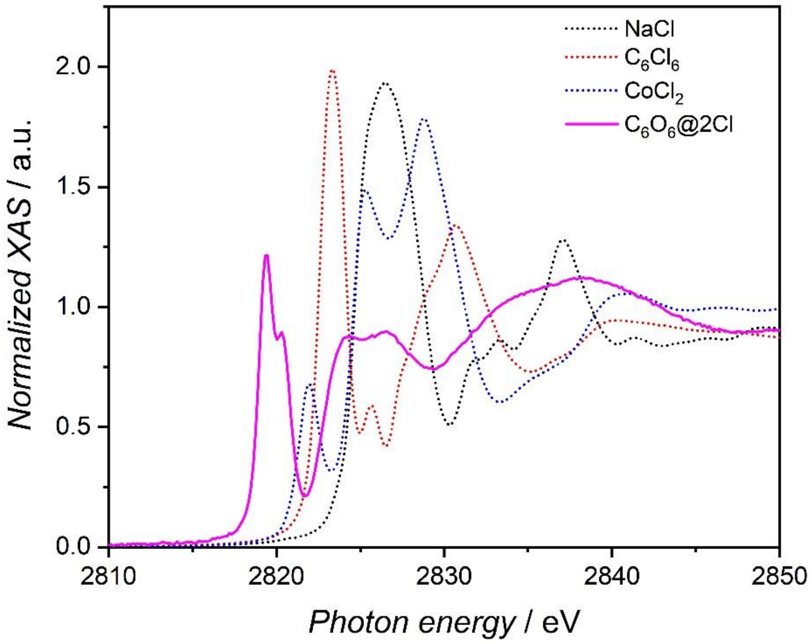

Figure 1. Comparison of XANES spectra at the Cl K-edge for various compounds showing different characteristics of the bond formed by the chlorine atom.

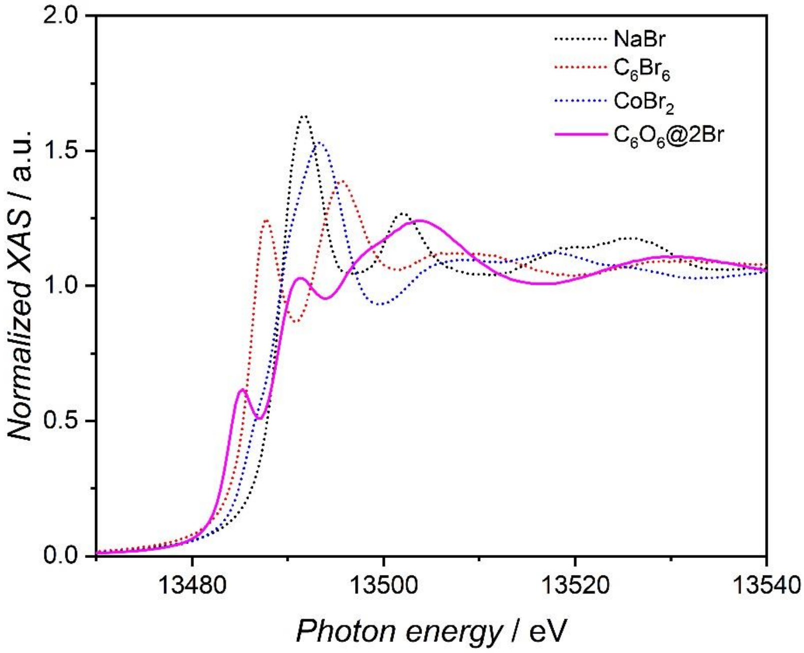

Figure 2. Comparison of XANES spectra at the Br K-edge for various compounds showing different characteristics of the bond formed by the bromine atom.

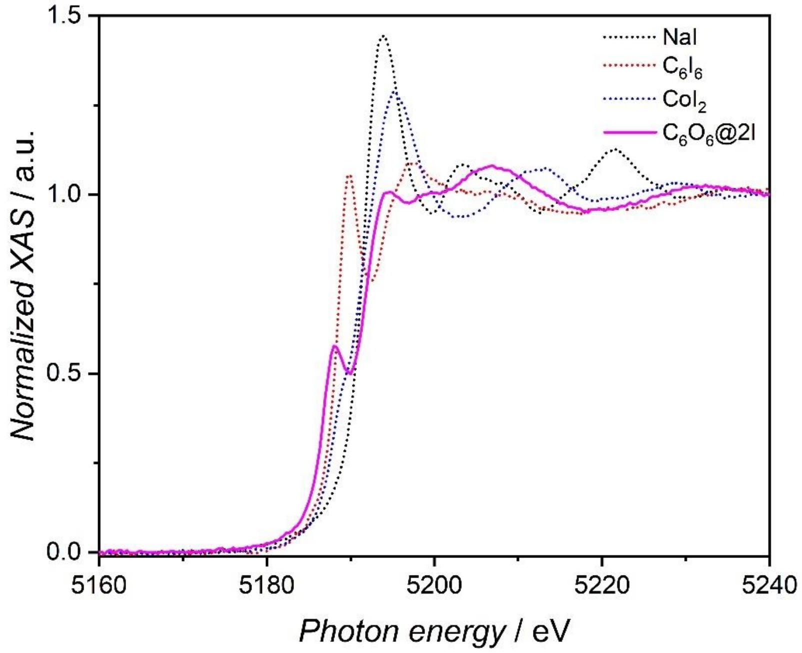

Figure 3. Comparison of XANES spectra at the I L_1-edge for various compounds showing different characteristics of the bond formed by the iodine atom.