ESRF	**Experiment title:** Exploration of X-ray magneto-chiral dichroism in lanthanide complexes with strongly chiral helicenes	**Experiment number**: CH-6926
Beamline: ID12	**Date of experiment**: from: 09.04.2024 to: 15.04.2024	**Date of report**: 21.06.2024
Shifts: 17	**Local contact(s)**: Andrei Rogalev	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Gabriela Handzlik*, Michał Magott*, Katarzyna Rzepka*, Wiktor Wolański*

Jagiellonian University, Faculty of Chemistry, Gronostajowa 2, 30-387 Kraków, Poland

Report:

The aim of the experiment CH-6926 was to screen the series of chiral compounds for X-Ray Natural Circular Dichroism (NCD) at room temperature (RT) and to choose the most promising candidates for series of XNCD, XMCD (X-Ray Magnetic Circular Dichroism) and XMChiD (X-Ray Magneto-chiral Dichroism) measurements at helium temperature.

From 09.04.2024 (16:00) to 11.04.2024 (18:00) a series of XNCD experiments was performed at room temperature for 16 different single crystals. We have tested the series of chiral propeller-like complexes based on the smallest helicene molecule (phendo) [Δ-[Ln(phendo)$_4$][Δ-[As(cat)$_3$]$_2$](NO$_3$)·5MeCN and (Λ,Λ) enantiomers (Ln = Tb, Dy, Er, Yb; phendo = 1,10-phenanthroline-*N*,*N'*-dioxide; cat = catecholate; MeCN = acetonitrile), optically pure complexes with bigger helicene ligand – [Ln(BHT)$_3$]$_2$((*P*)-(+)-azahelicene) (Ln = Er, Yb) and its second enantiomer (BHT = butylated hydroxytoluene) and two crystal phases of MnDAPNb 3-dimentional chiral network. Then, based on the results of XNCD measurements at RT, the most promising crystals were chosen for XMCD and XMChiD measurements at helium temperature. This type of measurements took much longer than XNCD at RT because XMChiD effect is in most cases weaker than XNCD and XMCD, therefore a lot of XAS spectra were required to be collected to see if any signal is observed for their difference. These measurements were performed from 11.04.2024 (18:00) to 14.04.2024 (morning) for one set of crystals (two enantiomers of the same compound, the most promising one, the same crystals that were tested at room temperature for XNCD). The last 24 hours were used for the trial with the pair of enantiomers of the different compound (in the magnetic field), even though we did not observe XNCD signal at RT for them during first two days of the beam time.

XNCD, XMCD and XMChiD were extracted from the collected XAS spectra as presented below. XNCD was calculated as a difference between XAS spectra measured for two different polarisations (the effect of magnetic field must be cancelled out if the magnetic field was applied).

$$NCD = \frac{XAS(P^+B^+) + XAS(P^+B^-)}{2} - \frac{XAS(P^-B^+) + XAS(P^-B^-)}{2}$$

XMCD signal is reversed by the change of magnetic field sign and by the change of light polarisation sign. Therefore it was calculated as presented below:

$$MCD = \frac{XAS(P^+B^+) + XAS(P^-B^-)}{2} - \frac{XAS(P^-B^+) + XAS(P^+B^-)}{2}$$

XMChiD is observed for the unpolarised light and changes sign with the change of the magnetic field sign. Therefore the spectra were calculated as below to cancel out the polarisation change effect:

$$MChiD = \frac{XAS(P^+B^+) + XAS(P^-B^+)}{2} - \frac{XAS(P^+B^-) + XAS(P^-B^-)}{2}$$

For XNCD measurements at RT, crystals were covered with small amount of apiezon N (to prevent loss of crystallization solvent molecules) and secured in the holder by polyethylene foil or Kapton. Non-zero XNCD

signals at room temperature have been obtained only for one type of compound *R*-MnDAPNb and *S*-MnDAPNb crystallizing in tetragonal space group $P4_12_12$. XNCD was measured at Mn K-edge (Figure 1).

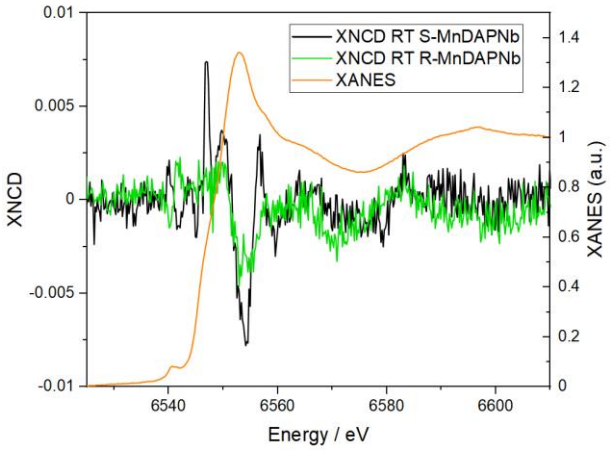

Figure 1. Two XNCD signals (at 6540 eV and at 6542 eV) for *S*- and *R*-MnDAPNb crystals at room temperature. Stronger signals on the graph does not change sign with enantiomer, they may be the result of decomposition of sample or diffraction peaks.

Based on the results of XNCD measurements at RT we have chosen *S*- and *R*-MnDAPNb crystals as the best candidates for the measurements in magnetic field at low temperature. Series of XAS spectra were collected at 3K at Mn K-edge for the exact same crystals that were measured at room temperature (Figure 2).

Figure 2. Holder for low temperature measurements in magnetic field with crystals *S*- and *R*-MnDAPNb.

For each enantiomer two different positions at the crystal were measured using circularly polarized beam (first position at one crystal was getting visibly destroyed in the end of the series of measurement):

- 1st position: 24 scans at +17 T (two different polarizations – 2 x 12 scans),
- 1st position: 24 scans at -17 T (two different polarizations – 2 x 12 scans),
- 2nd position: 16 scans at +17 T (two different polarizations – 2 x 8 scans),
- 2nd position: 8 scans at -17 T (two different polarizations – 2 x 4 scans).

Different XNCD signals were registered in 1st and 2nd position due to different orientation of crystals (Figure 3 a,b,c). Similar XMCD spectra were obtained for both positions of crystals (Figure 3 d,e). No XMChiD was observed (only decomposition of the sample was visible). The series of measurements using linear light polarization was tested (20 scans at +17 T (two different polarisations – 2 x 10 scans) and 20 scans at -17 T (two different polarisations – 2 x 10 scans)), but no XMChiD signal was observed.

We have also measured low temperature XANES spectra at Dy L_3-edge for [Δ-[Dy(phendo)$_4$][Δ-[As(cat)$_3$]$_2$](NO$_3$)·5MeCN and (Λ,Λ) enantiomer. Measurements were done for new crystals because the ones from XNCD measurements at room temperature lost solvent molecules after a few days out of mother liquor. Measurements at low temperature were done for one position at each crystal:

- 16 scans at +17T (two different polarizations – 2 x 8 scans),
- 16 scans at -17 T (two different polarizations – 2 x 8 scans).

As a result we obtained weak XNCD signal (if we consider the background is far away from flat line). The crystals decomposed during the measurements (visible changes in succeeding XANES spectra at the same light polarization and magnetic field). Results are presented in Figure 4.

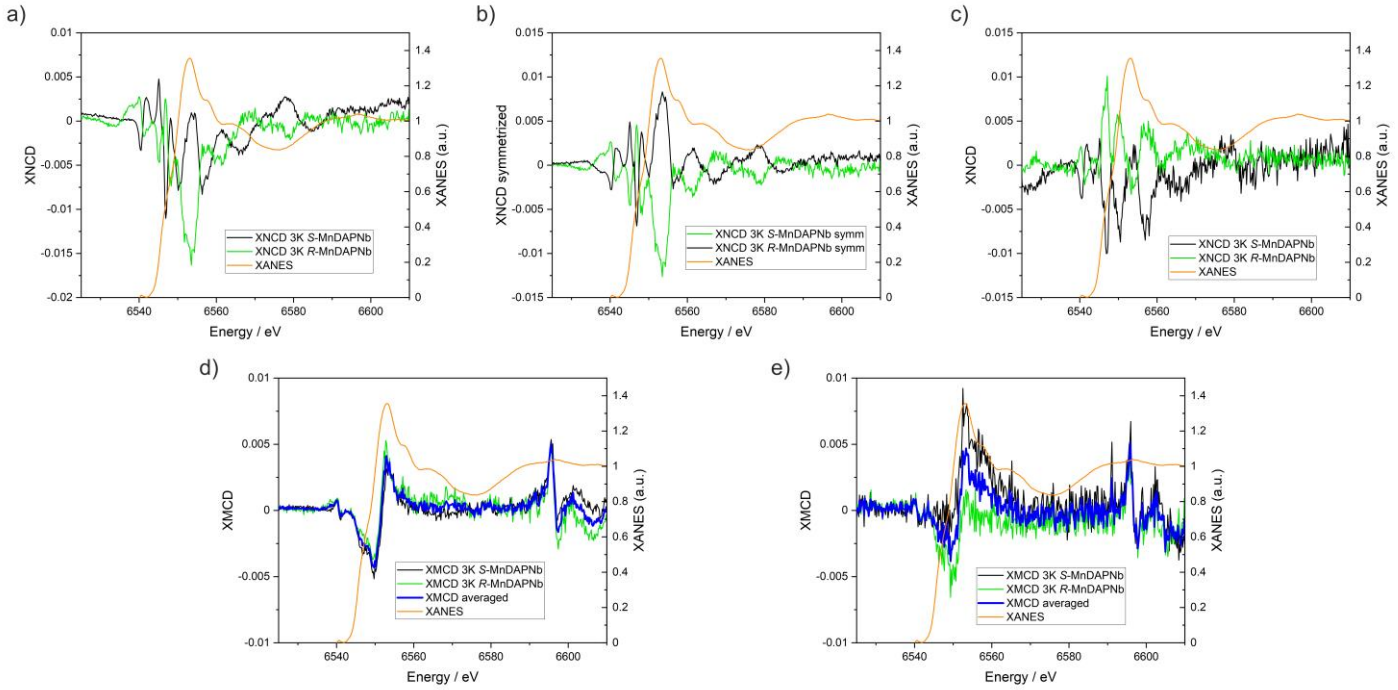

Figure 3. Mn K-edge, MnDAPNb: a) XNCD 1st position, b) NCD 1st position symmetrized, c) NCD 2nd position, d) MCD 1st position, e) MCD 2nd position.

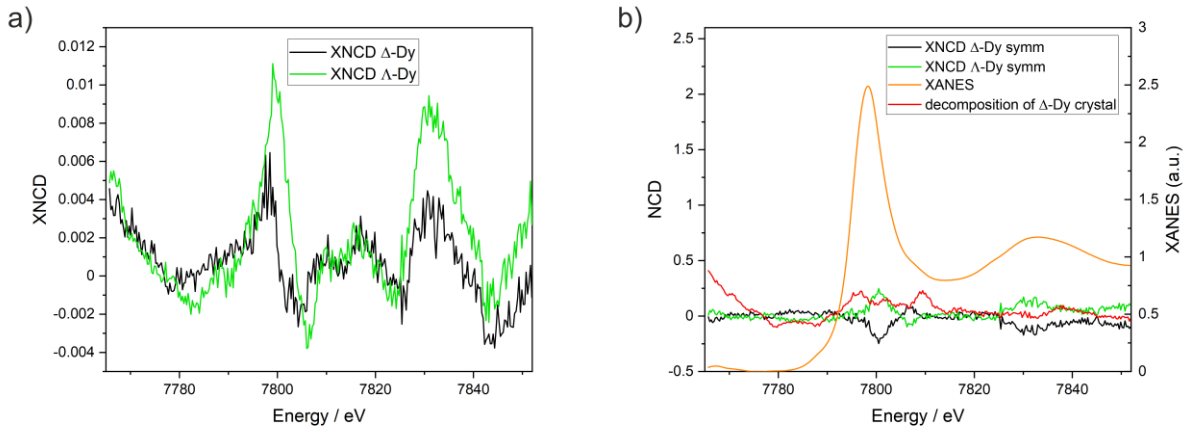

Figure 4. Dy L_3-edge, [Δ-[Dy(phendo)$_4$][Δ-[As(cat)$_3$]$_2$](NO$_3$)·5MeCN (Δ-Dy) and (Λ,Λ) enantiomer (Λ-Dy): a) XNCD; b) XAS, XNCD symmetrized, decomposition (difference between first and last XAS spectra at the same field and polarization) during measurement;

The results of CH-6926 experiment provides a basis for future XNCD, XMCD and XMChiD measurements. Next measurements should be planned for the chiral crystal of preferably high symmetry of the crystal structure for easier orientation of the crystals in respect to the incoming beam. Few different orientations of the crystal should be tested, as the shape of signals and the strength of these effects depends on the crystal orientation. These kind of measurements may require acquisition of many XANES spectra due to the weakness of XMChiD effect. The important things to keep in mind are: possible degradation of the crystal by X-ray beam during the measurement and possible diffraction peaks at some orientations of the crystal (the position and intensity of the diffraction peak may differ during the series of XANES spectra measurements). Both these problems may significantly hinder the XMCD or XMChiD spectra extraction.