

Proposal Code CH-4457**Proposal Title X-ray Magnetochiral Effect in an Enantiopure Molecular Paramagnet****Goals, experimental set-up and background**

CH-4457 is a continuation of project CH-4171 dedicated to the XNCD, XMCD and XM χ D investigation of chiral transition metal complexes, with the goal of observing the magnetochiral effect in discrete molecules for the first time. CH-4171 was devoted to the study of a chirally-resolved helicoidal extended cobalt chain (Δ -**1** and Λ -**1**). Chiral crystals of both Δ and Λ enantiomers were isolated and we obtained clear and reproducible XNCD spectra for both enantiomers. However, we were unable to obtain unambiguous XMCD or XM χ D spectra, possibly due to the small magnetic moment of the studied compound ($S = 1/2$ per molecule) and/or the spin delocalization over the cobalt ions. Therefore, we decided to turn our attention to the chiral chromium analogue. This compound should have all the advantages of **1**, particularly a strong XNCD signal, but with a higher magnetic moment ($S = 2$) allowing us to obtain XMCD and XM χ D spectra.

ID12 is equipped with an undulator supplying circularly polarized hard X-rays. It has two hutches; one allows the measurement of XANES spectra at room temperature for acquisition of X-ray natural circular dichroism (XNCD) spectra and to study the angular dependence of the spectra on single crystals, thanks to a rotating sample holder. The second hutch allows the acquisition of XANES spectra at cryogenic temperatures (≥ 2 K) in the presence of a magnetic field ($\leq |17$ T|), for the analysis of XNCD, X-ray magnetic circular dichroism (XMCD) and X-ray magnetic chiral dichroism (XM χ D). Our experiments, outlined below, were performed at the K edge of chromium and cobalt.

Results

Chromium chains. One crystal each of chromium chain **2** ($350 \times 300 \times 200 \mu\text{m}^3$) and of **3** ($200 \times 150 \times 150 \mu\text{m}^3$) were selected. The chromium concentration $[\text{Cr}] = 15.89\%$ (**2**) and 13.26% w/w (**3**). The crystals were mounted on a cold finger and measured at 2 K under a field of ± 17 T in a series of 12 pairs (left and right polarizations) for each field direction. In this way XANES spectra were recorded, from which XNCD, XMCD and XM χ D spectra were derived.

Unfortunately, neither crystal gave a non-zero XNCD signal (Fig. 1), suggesting that the compounds did not crystallize in a chiral space group. Interestingly, the two compounds gave quite different XANES

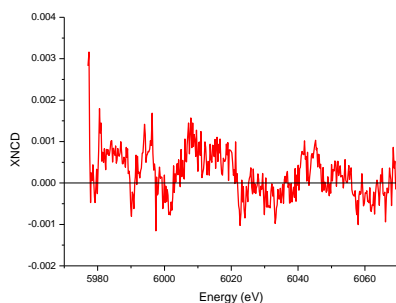


Fig. 1. XNCD spectrum of **3**.

spectra. Indeed, the principal difference between the two molecular systems is found in the delocalization of the spin over the polynuclear core: in **3**, the spin is delocalized over the metal centers, while in **2**, the spin is localized on one metal ion. While an XMCD signal was observed for **2**, it was not present for **3**, consistent with the delocalized character of the spin, as previously noted in the case of delocalized **1**. The angular dependence of the absorption spectra remains to be studied.

Concerning the synthetic issues, we had no difficulty in obtaining the racemic starting material as expected, and we were confident that we could chirally resolve the chromium chains by using the same procedure used for the cobalt analogue **1**. However, we found that the anion exchange reaction did not proceed as expected. Indeed although the starting cobalt and chromium compounds are almost identical from a molecular point of view, the interaction of the two

enantiomers with the chiral resolving agent was found to be completely different; selective for cobalt and unselective for chromium. An experienced synthetic postdoc will join our team in April 2016 to study the chiral resolution of chromium chains full time, through ligand and anion modification.

In order to make the best use of the remaining beamtime we adapted our program to focus on obtaining XANES spectra on an alternative chirally-resolved coordination compound **4**, and completed the study of the angular dependence of the XNCD of **1** for publication of the work performed in CH-4171.

Chiral cobalt coordination complexes. Complex **4** is a chiral cobalt coordination complex for which the two enantiomers, Δ and Λ , have been isolated. Crystals of each enantiomer were selected (Δ -**4**: 2.0 x 1.5 x 1.5 mm³, Λ -**4**: 1.0 x 0.5 x 0.5 mm³; [Co] = 12.01%) and mounted on the cold finger and measured at 2 K under a field of ± 17 T in a series of 12 pairs (left and right polarizations) for each field direction. Strong (~ 2.5 %) and mirror-image XNCD signals for the two enantiomers, and a clear XMCD (~ 0.2 %) signal were observed. An evolution of the signal with time was observed during data treatment, which although small ($\sim 0.15\%$), interfered with any XMCD signals that may have been present. The angular dependence of the absorption spectra and the magnetization with field remain to be studied.

Angular dependence of the XNCD of cobalt chains. In CH-4171, we observed that cobalt chains Δ -**1** and Λ -**1** demonstrated a clear angular dependence of the XANES spectra, when mounting the crystals with the *c* axis either parallel (0°) or perpendicular (90°) to the X-ray beam. This strong linear dichroism was unexpected and we were not prepared to fully study this phenomenon during CH-4171. For this reason, the preliminary data acquired during CH-4171 was not publishable. After data analysis and indexing of the crystal faces at our home institutions, we were in a position to understand and anticipate the evolution of the spectra according to group theory considerations. Therefore, in CH-4457, we carefully studied the evolution of the XANES and XNCD spectra with respect to rotation around the *z* laboratory axis in several samples. Several small plate-like crystals of Δ -**1**, Λ -**1**, ([Co] = 7.69%) as well as the new *rac*-**5** ([Co] = 9.03%) were selected and mounted either flat or on their edge on a 5-well sample holder at room

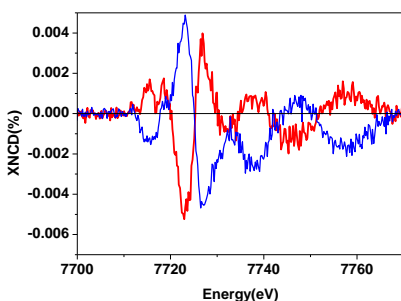


Figure 2. XNCD for Δ -**1** (red) and Λ -**1** (blue) with the beam 45° from normal.

temperature. Starting with a crystal oriented with the *c* axis parallel (0°) to the X-ray beam and rotating out of collinearity ($0^\circ \rightarrow 45^\circ$) with the beam, we observed a gradual modification of the XANES spectrum. Likewise, when we rotated a crystal oriented perpendicular (90°) to the X-ray beam towards collinearity ($90^\circ \rightarrow 45^\circ$), we observed a modification of the spectrum converging to an identical spectrum as above at 45° . XNCD spectra were plotted for 0° , 45° (Fig. 2) and 90° ; while they were reversed for each set of enantiomers as expected, the XNCD also showed an unexpected angular dependence, suggesting the presence of more than one component. This result is not consistent with the symmetry of the point group previously determined by X-ray crystallography (422), causing us to revise our crystallographic interpretation. This is a beautiful demonstration of how the sensitivity of X-ray absorption can refine the interpretation of X-ray diffraction data. It should also be mentioned that, although *rac*-**5** crystallizes in a completely different space group than Δ -**1** and Λ -**1**, a similar spectral evolution was observed. This phenomenon can be linked to the orientation of the metal axis of the molecules with respect to the incident beam. This study has been completed and the manuscript is currently being finalized.