ESRF	**Experiment title:** Magnetochiral dichroism in polynuclear coordination compounds	**Experiment number**: **CH-4460**
Beamline: ID12	**Date of experiment**: from: 27/01/2016 to: 02/02/2016	**Date of report**:
Shifts: 18	**Local contact(s)**: Fabrice Wilhelm, Andrei Rogalev	*Received at ESRF:*

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Report:

After our successful investigation of Co-radical helices to exhibiting strong Magneto-chiral dichroism at the metal K-edge[1] and the unsuccessful attempt to evidence a similar phenomenon in lanthanide helices[2] the systems investigate in this new session of measurements comprise chiral polynuclear transition metal ions.

The first investigated system comprises the two enantiomeric forms of $\{Tb[Ni(pro)_2]_6\}^{3+}$ where pro is L,D-prolinate. The focus was here on the chiral Ni sites and the investigation was performed at the K edge.
The structure is shown in Fig. 1a. The low temperature XMCD and XMχD signals are shown in Figure 1b and 1c for the L- and D- derivatives, respectively. A pronounced magnetic response at the pre-edge (ca 8335 eV) is observed, in analogy with what observed for Co and Mn helices.The L derivatives showed also a pronounced magneto-chiral response, whose aspect was however quite suspicious, as the major contribution was not observed at the pre-edge. Further investigation of the D derivative revealed a similar XMCD response but the magnetochiral signal was not showing the parity effect that is expected on the basis of symmetry consideration (Fig. 1c). The detected magnetochiral dichroism resulted to be a spurious effect, as well demonstrated by the superposition of the XMχD signal over the derivative of the XNLD one shown in Fig. 2d.
The second type of system we investigated chiral extended metal atom chain (EMAC) compound made up of 5 antiferromagnetically coupled Ni ions, whose structure is depicted in Figure 2a. Both enantiomers showed weak XMCD response at the Ni K edge at low temperature (Figure 2b). Unfortunately, no single crystals could be obtained for the two samples, so XNCD could not be measured on the orientationally averaged powder sample. Low temperature XMχD measurements were attempted on the pressed pelled of the powdered samples, but gave no significant results.

We then performed additional measurement on the original Co-radical helix system with the aim to evidence that a photon-intensiity dependent magnetic hysteresis is detectable at the Co K-edge, in agreement with the "Single Chain Magnet" behavior of the compound. Interestingly the same sample did not reveal any hysteretic behavior at the L-edge. This study evidences the dramatic effect of defects present on the surface to suppress the slow dynamics of the magnetization, a feature associated to the strict one-dimensional character of the magnetic bistability. A manuscript is in preparation on this topic..

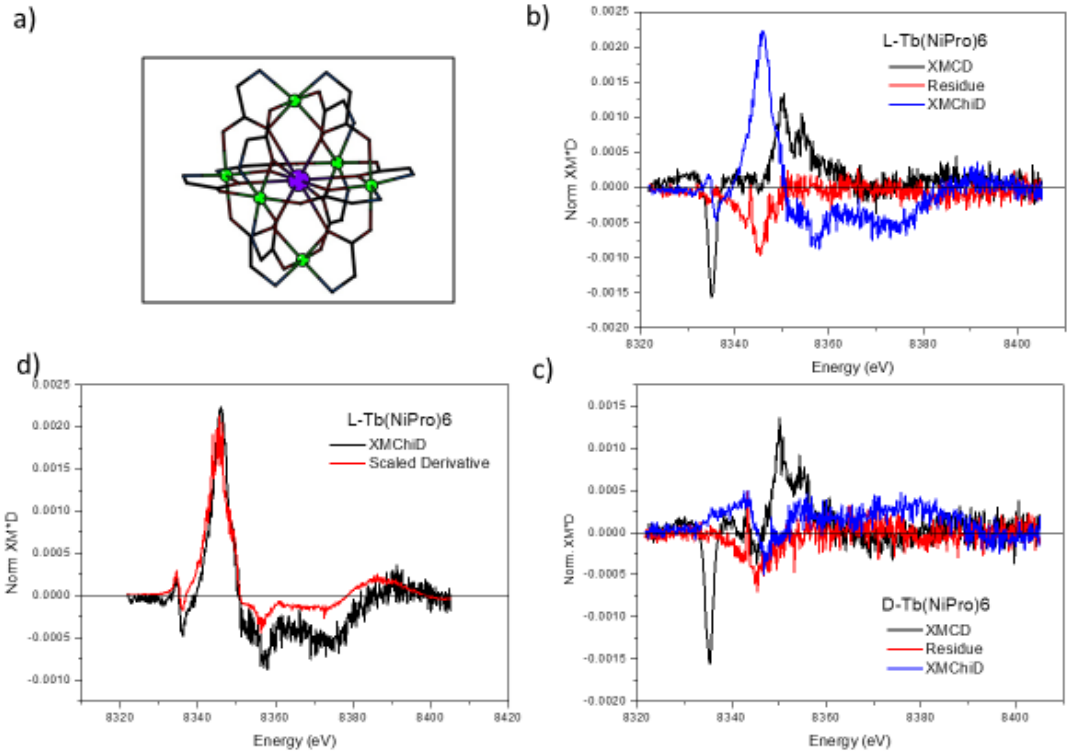

Figure 1. *a) View of the LnNi6 clusters built by prolinate ligands (Ln, violet; Ni, green; organic ligands have been represented partially for the sake of clarity. b) , c) , d)*

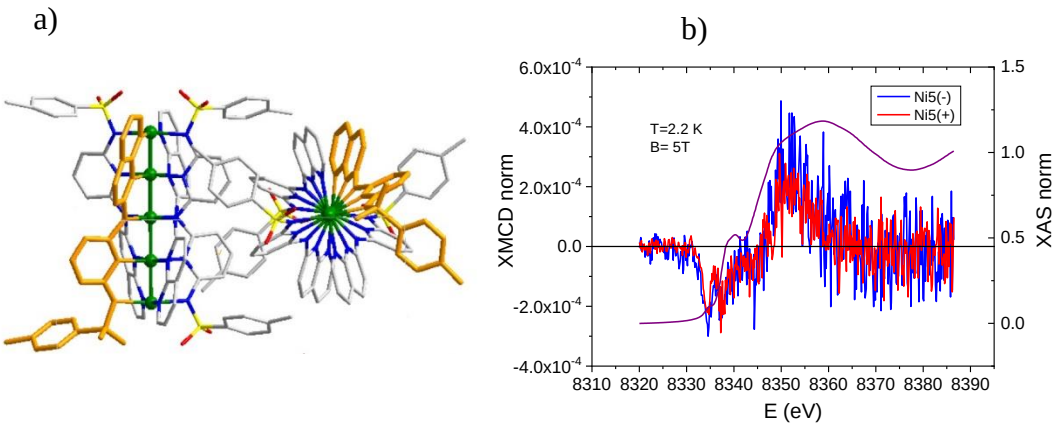

Figure 2. *Near edge X-ray absorption spectrum (XANES) at the L3 edge of Dy measured at room temperature in zero field (black line) obtained as* $1/2(\sigma^r+\sigma^l)$ *and X-ray natural circular dichroism spectra given by* $(\sigma^r-\sigma^l)$ *for two enantiomeric crystals.* σ^r *and* σ^l *denotes x-ray absorption cross section for right- and left- circularly polarized X-rays, respectively.*

References

1 Sessoli, R., Boulon, M.-E., Caneschi, A., Mannini, M., Poggini, L., Wilhelm, F. & Rogalev, A. Strong magneto-chiral dichroism in a paramagnetic molecular helix observed by hard X-rays. *Nat Phys* **11**, 69-74, (2015).

2 Mihalcea, I., Perfetti, M., Pineider, F., Tesi, L., Mereacre, V., Wilhelm, F., Rogalev, A., Anson, C. E., Powell, A. K. & Sessoli, R. Spin Helicity in Chiral Lanthanide Chains. *Inorg. Chem.* **55**, 10068-10074, (2016).