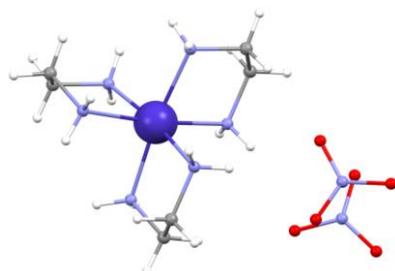




	Experiment title: A systematic study of the influence of electron configuration on X-ray magnetochiral and natural circular dichroisms in a series of isostructural chiral coordination complexes	Experiment number: CH-5531
Beamline: ID12	Date of experiment: from: 09/11/2018 to: 13/11/2018	Date of report: 29/02/2020
Shifts: 9	Local contact(s): Andrei Rogalev, Fabrice Wilhelm	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Elizabeth Hillard, CNRS* Patrick Rosa, CNRS* Philippe Saintavit, Sorbonne Universités* Miguel Cortijo, CNRS* Angela Valentin-Perez, University of Bordeaux*		

This project was focused on the recording of different dichroisms in chiral paramagnetic molecules: natural circular dichroism, magnetic circular dichroism and magnetochiral dichroism, all measured at the metal K-edge. Magnetochiral dichroism (MChD), is a particularly exotic phenomenon, and is a leading mechanism to explain natural homochirality. It is manifested by the differential absorption of non-polarized light by chiral matter as a function of the direction of an external magnetic field. Although this effect was predicted in the 1960s,¹ there have been only a few experimental observations, mostly in the UV-visible range.² In order to detect this exceedingly rare phenomenon in the X-ray range (XMChD), we proposed a work program centered around a series of chiral $[M(en)_3](NO_3)_2$ coordination complexes. These compounds are not only interesting candidates for the discovery of XMChD in discrete molecules (as yet undocumented), but all of these complexes are expected to exhibit strong X-ray natural circular dichroism (XNCD) at the metal K-edge. Another advantage of these compounds is that they can be synthesized with different transition metals, and therefore an isostructural series of such compounds, but with different electronic structures and spin states, can be obtained. The ID12 of the ESRF is the world leader in the field of X-ray optical activity, being the only source technically capable of measuring these fundamental phenomena at the metal K-edge.

Experimental evidence of XMChD has to date been only been detected in extended structures.^{3,4} Most notably, XMChD was recently observed in a chiral cobalt coordination polymer,⁴ but not yet in discrete molecules. The paucity of examples is likely due to several reasons. XMChD arises from electric dipole (E1, parity odd)-electric quadrupole (E2, parity even) interference, it exists only in space-time parity odd ordered media, such as a non-centrosymmetric magnetic single crystals. The XMChD effect is expected to be very small and therefore can only be measured at the ESRF ID12, due to high degree of circular polarization and beam stability found at this beamline. Theoretically, the effect can be maximized by using highly chiral compounds, with at least three-fold or higher crystal symmetry and a magnetically degenerate ground state, and thus, transition metal complexes seem particularly well-suited.⁵



Crystal structure of $[Co(en)_3](NO_3)_2$

For this study, we prepared an isostructural series of $[M(en)_3](NO_3)_2$ complexes ($M = Mn^{II}, Co^{II}, Ni^{II}, Zn^{II}$; en = ethylenediamine), with *d*-orbital occupancies of 5, 7, 8 and 10 electrons, respectively. They crystallize in the high symmetry $P6_322$ space group as a conglomerate, that is, a mechanical mixture of delta and lambda crystals.⁶ This symmetry is ideal for XNCD and XMChD experiments, as the dichroism spectra will not be adulterated with other dichroic effects with proper crystal alignment. The objectives of this study were to: 1) to study the evolution of the XNCD spectral shape and

intensity as a function of the 3d electron count, and 2) to detect and study the evolution of the XMChD signals across the series of compounds as a function of their spin state and magnetic anisotropy.

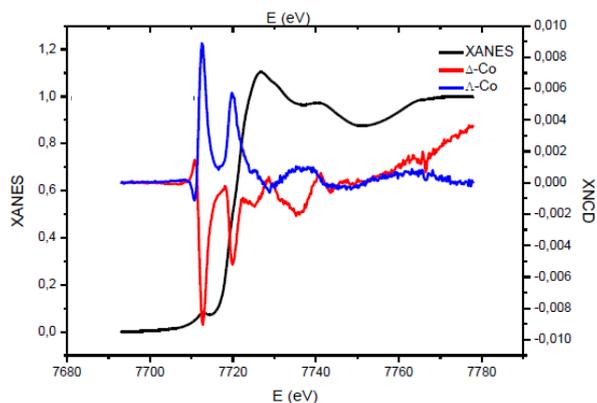
XNCD measurements at room temperature were performed on all of the compounds, revealing mirror-image spectra for the two enantiomers, delta and lambda (see Figure for an example). The spectra were obtained by collecting twelve pairs of X-ray absorption spectra using right- and left- circular polarizations. The XNCD spectra were then obtained from taking the difference between the two, and plotted as a function of energy. In the XNCD, a variety of dichroism peaks could be identified, in the pre-edge, rising edge and post-edge regions. The pre-edge signals Co(II) and Ni(II) were very large, reaching about 1% of the X-ray absorption spectrum. Interestingly, the pre-edge signals for the Mn(II) analogue were significantly lower, and the signs of the peaks were reversed for the two enantiomers, compared to those of Co and Ni. We do not as yet have an explanation of the anomalous Mn(II) response, and this will require further study and confirmation. The number of pre-edge features is consistent with the 3d-orbital occupancy. For example, in the Ni(II) analogue shown, the vacancies in the two energy levels of the octahedrally-split valence orbitals result in two pre-edge features. On the other hand, the Zn(II) analogue, having no vacancies in the 3d shell, does not exhibit any pre-edge features, but rather only transitions to higher-energy virtual orbitals. The XAS of powder samples were also measured to provide a self-absorption correction. These data are currently being used to develop algorithms to model XNCD spectra with a co-proposer, and are expected to be submitted for publication at the end of 2020.

Preliminary XMCD and XMChD spectra were obtained for the Co(II), Ni(II) and Mn(II) analogues at 1.9 K under a magnetic field. The magnitude of the required field was determined by obtaining saturation curves by plotting the intensity of the magnetic circular dichroism peak maximum as a function of field. We were able to verify that no XMChD signal could be observed in the Ni(II) case. However, non-zero XMChD spectra for the Co(II) and Mn(II) compounds suggested that these compounds may be XMChD-active. However, we only had enough time to obtain spectra from only one enantiomer from each compound. Without mirror-image data from the opposite enantiomer, it is impossible to validate that the signal indeed arises from the XMChD phenomenon. We hope to continue these experiments.

Finally, we were able to use the XNCD response of the Co(II) and Ni(II) compounds in a mapping of the handedness of an assembly of crystals. As mentioned above the $[M(en)_3](NO_3)_2$ complexes represent a rare case where the two enantiomers segregate themselves upon crystallization. Knowing the handedness of individual crystals in a mixture is not a trivial matter, and is most often done using X-ray diffraction, which is time-consuming. Optical solid-state analysis of chirality in the solid state is challenging,⁷ because linear dichroism and birefringence can be orders of magnitude more intense than the circular dichroism signal. However, in XNCD, the birefringence artefacts disappear, and the linear dichroism can be obviated by orientation of the crystals, which is not difficult with high symmetry groups such as the present one. By setting the X-ray energy to that of the pre-edge, and restricting the beam spot size to $150 \times 50 \mu m^2$, the absorption with right and left circularly polarized light was obtained. The difference between the two absorptions, being either negative or positive, revealed the handedness of the crystal where the data was taken. These results have been submitted to a peer reviewed journal.

References

1. M. P. A. Groenewege, *Molec. Phys.*, 5 (1962) 541-563.
2. a) G. L. J. A. Rikken, *et al.*, *Nature*, 390 (1997) 493; b) P. Kleindienst, G. H. Wagnière, *Chem. Phys. Lett.* 288 (1998) 89-97. c) M. Vallet, *et al.*, *Phys. Rev. Lett.* 87, (2001) 183003; d) M. Kubota, M. *et al.*, *Phys. Rev. Lett.* 92 (2004) 137401; e) C. Train, *et al.* *Nature Mater.* 7 (2008) 729; f) Y. Kitagawa, *et al.* *Angew. Chem. Int. Ed.* 50 (2011), 9133; g) M. Ceolín, *Adv. Mater.* 24 (2012) 3120.
3. J. Goulon, A. Rogalev, F. Wilhelm, *et al.*, *Phys. Rev. Lett.* 88 (2002) 237401.
4. R. Sessoli, M-E. Boulon, A. Caneschi, *et al.* *Nat. Phys.*, 11 (2015) 69.
5. G. Wagnière, *Chem. Phys.*, 245 (1999) 165-173.
6. P. V. Bernhardt, M. J. Riley, *Aust. J. Chem.* 56 (2003) 287.
7. W. Kaminsky, K. Claborn, B. Kahr, *Chem. Soc. Rev.* 2004, 33, 514.



XNCD spectrum of $[Ni(en)_3](NO_3)_2$.