

## Proposal Code CH- 4171

Proposal Title X-ray MagnetoChiral Effect in an Enantiopure Molecular Paramagnet

### Goals and experimental method

The overall goal of the proposal was to observe the magnetoChiral effect for the first time in a discrete molecule,  $\text{Co}_3(\text{dpa})_4(\text{MeCN})_2\text{X}$  (where X = a dianion, **1**). The experiment was divided in two parts. Firstly we planned to use room temperature XNCD at the K-edges of Co to select crystals of each molecular chirality ( $\Delta$ -**1** and  $\Lambda$ -**1**) and to verify that the selected crystals were indeed chiral and not twinned. The second part of the experiment was concerned with the XMCD and XM $\chi$ D measurements at the Co K-edge in the presence of a magnetic field at cryogenic temperatures.

XMCD at the K-edge is proportional to the orbital magnetization, XM $\chi$ D is a measure of orbital anapole or toroidal moment of the orbital currents, while the integral of the XNCD at the K-edge is proportional to the effective operator comprising both orbital magnetization and orbital anapole. Careful analysis of all dichroism spectra in the X-ray range should help us to elucidate the role of orbital magnetism in chiral molecular paramagnets.

### Results

**General considerations and XNCD measurements:** We brought with us crystals of opposite enantiomers of the linear trinuclear compound  $\text{Co}_3(\text{dpa})_4(\text{MeCN})_2\text{X}$  (where X = a dianion, **1**), formed by two different crystallization techniques (**A** and **B**). We observed that the crystallization technique **A** gave very thin crystals with a low signal response, while technique **B** gave crystals with an acceptable signal to noise ratio. We also observed considerable radiation damage to the crystals, and thus determined an X-ray flux where a compromise could be made between crystal degradation and signal to noise ratio. We also adapted the experimental sequence to normalize for radiation damage. Finally we were able to work out a proper mounting technique, using a five-well sample holder, immersion oil, and kapton tape.

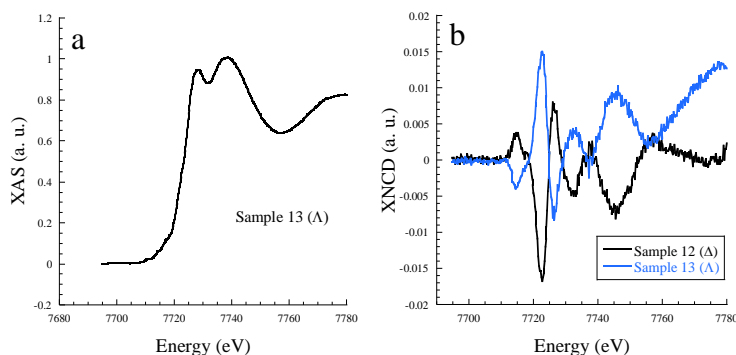


Figure 1. (left) XAS spectrum for a representative crystal, the  $\Delta$  enantiomer (the  $\Lambda$  enantiomer appears similarly),  $c$  parallel to X-ray beam; (right) XNCD spectra for two opposite enantiomers,  $c$  parallel to X-ray beam.

We obtained reproducible X-ray absorption spectra on the K-edge of Co for at least two crystals of each enantiomer (Figure 1a). By switching the polarization of the X-rays, and by examining the differences between the XAS spectra, we were able to obtain XNCD spectra confirming that the studied crystals were indeed chiral. Furthermore, we were able to verify that we indeed possessed crystals of opposite chiralities, based on the observation of opposite XNCD spectra according to the chirality of the crystal (Figure 1b). Thus the first goal of the project was met.

By mounting the crystals with the  $c$  axis either parallel ( $0^\circ$ ) or perpendicular ( $90^\circ$ ) to the X-ray beam, we could observe a clear angular dependence of the XAS as well as the XNCD spectra. It should be mentioned that the  $c$  axis of the crystal structure is coincident with the metal-metal bond axis of **1**. When the  $c$  axis of the crystal unit cell was oriented parallel with the X-ray beam, we observed XAS and XNCD

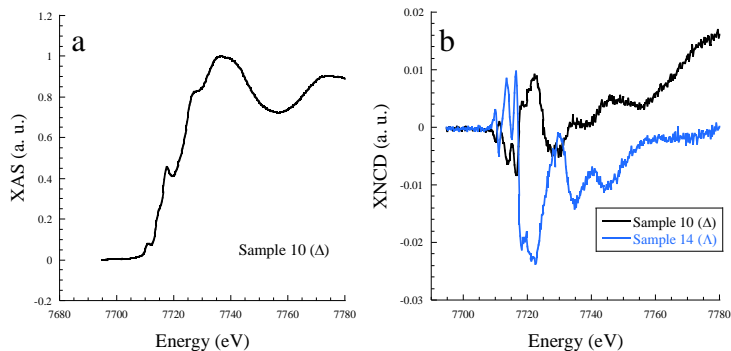


Figure 2. (a) XAS spectrum for a representative crystal, the  $\Delta$  enantiomer (the  $\Lambda$  enantiomer appears similarly),  $c$  perpendicular to X-ray beam; (b) XNCD spectra for two opposite enantiomers,  $c$  perpendicular to X-ray beam.

peaks in the perpendicular spectrum. Although we once again see opposite XNCD spectra associated with crystals of opposite chirality, the sign is reversed compared to what is observed when the crystal is in a parallel orientation (Figure 1). It should be emphasized that the visually apparent differences in the XAS (Figure 1a vs. Figure 2a) are due not to chirality, but to orientation, that is whether the X-ray beam is parallel or perpendicular to the metal-metal bond.

In order to confirm these preliminary findings, we studied the evolution of the spectra with respect to rotation around the  $y$  laboratory axis.

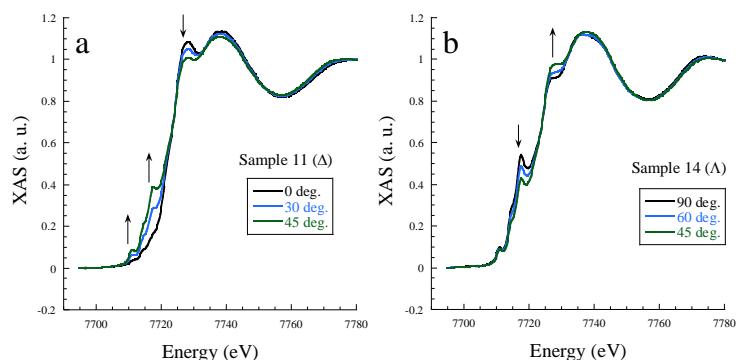


Figure 3. (a) XAS spectra for a crystal with a starting orientation parallel to the X-ray beam; (right) XAS spectrum for a crystal with a starting orientation perpendicular to the X-ray beam.

spectra such as those seen in Figure 1. However, when the  $c$  axis was oriented perpendicular to the X-ray beam, we observed different XAS spectra and XNCD spectra (Figure 2). In particular, in the XAS spectra, we notice an increase in the peaks at 7711 and 7718 eV, and a decrease of the peak at 7727 eV, with respect to the spectra of the crystal oriented parallel to the X-ray beam. Furthermore, the XNCD spectra are quite different; most notably the single peak seen at 7715 eV in the parallel spectrum is split into four

peaks in the perpendicular spectrum. Starting with a crystal oriented with the  $c$  axis parallel ( $0^\circ$ ) to the X-ray beam (Figure 3a), and rotating out of collinearity with the beam ( $0^\circ \rightarrow 45^\circ$ ), we observed a gradual increase of the XAS peaks at 7711 and 7718 eV and a decrease at 7727 eV. Likewise, when we rotated a crystal oriented perpendicular ( $90^\circ$ ) to the X-ray beam towards collinearity ( $90^\circ \rightarrow 45^\circ$ ), we observe a decrease of the XAS peak at 7718 eV and an increase at 7727 eV.

**XMCD/XM $\chi$ D measurements:** After verifying that we had crystals of opposite chirality on hand, we turned our attention to the magnetic measurements. This experiment is done in the presence of a magnetic field ( $H^+$  or  $H^-$ ) and the presence of circularly polarized X-rays ( $\phi^+$  or  $\phi^-$ ). The XMCD signal is the given by the following equation:

$$\frac{1}{2}[(\phi^+ - \phi^-)_{H^+} - (\phi^+ - \phi^-)_{H^-}]$$

While XM $\chi$ D is given by:

$$\frac{1}{2}[(\varphi^+ + \varphi^-)_{H^+} - (\varphi^+ + \varphi^-)_{H^-}]$$

We first performed a full measurement of one enantiomer ( $\Lambda$ ) at 2 K in a 4 T magnetic field. In this experiment, we were unable to see a clear XMCD signal (Figure 3a), but a (quite noisy) XM $\chi$ D signal could be discerned (Figure 3b).

Due to the weakness of the signals, we decided to perform the same experiment, but at 17 T, to possibly enhance the magnetisation. However, due to some technical problems (instability of the temperature, sample loss, and lack of helium, we were unable to collect a full data set at 17 T. We were not able to see a clear XMCD or XM $\chi$ D signal based on these limited data.

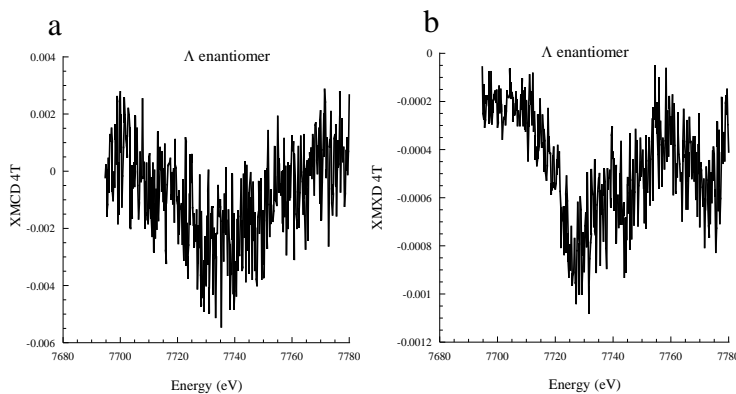


Figure 3. (a) XMCD spectrum a sample of the L enantiomer at 4 T; (b) XM $\chi$ D of the same sample at 4T.

## Conclusions

In this project, we reached our first goal in obtaining XNCD spectra for both enantiomers of the chiral compound  $\text{Co}_3(\text{dpa})_4(\text{MeCN})_2\text{X}$ . It should be mentioned that this is the first time that chiral compounds with metal-metal bonds have been enantiomerically resolved and is one of the few examples of XNCD on any kind of molecular compound. We were able to obtain XNCD for both enantiomers in an orientation where the  $c$  axis is parallel to the X-ray beam, and when it is perpendicular to the X-ray beam. We were also able to chart the evolution of the XAS spectra with angle.

Unfortunately, we were not able to obtain XMCD or XM $\chi$ D spectra of the studied samples. It is unclear at this moment if the marginal preliminary data are a result of the small magnetic moment of the studied compound ( $S = 1/2$  for  $\text{Co}_3(\text{dpa})_4\text{X}$ ). This point should be confirmed in the future. If the problems prove to be intrinsic to the compound, it may be worthwhile to investigate instead the more magnetic chromium analogue  $\text{Cr}_3(\text{dpa})_4\text{X}$  ( $S = 2$ ).