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The global objective of this project was to acquire experimental data to use in the development of tools to simulate XNCD spectra. The proposed systems were designed to address fundamental questions regarding the influence of symmetry on the XNCD response, specifically in probing the influence of molecular and crystal symmetry around the absorbing atoms. To do so, we planned to examine the two crystal enantiomorphs of six nickel complexes, all crystallizing in Sohncke space groups, compulsory for a chiral arrangement of atoms. This chirality can be either 1) intrinsically molecular, 2) due to the crystal environment or 3) both.

The proposed compounds are as follows: crystals containing a 1) **chiral-at-nickel** complex, with the metal on the **principal symmetry crystal axis**, Nickel-doped tris(2,2'-Bipyridyl)-Zn(II) bis(hexafluorophosphate), 2) **chiral-at-nickel** complex, with the metal on a **general position**: tris(2,2'-bipyridyl)-nickel(II) chloride tartrate dodecahydrate, 3) an **achiral** nickel complex, with the metal on the **principal crystal symmetry axis**: hexaaqua-nickel(II) sulfate, and nickel-doped bis(2,2':6',2''-terpyridyl)-manganese(II) diperchlorate hemihydrate, and 4) an **achiral** nickel complex, with the metal on a **general position**: hexa-aqua-nickel(II) bis(camphor-10-sulfonate), and bis(2,2':6',2''-terpyridyl)-nickel(II) bis(hexafluorophosphate). For the achiral nickel compounds, the crystal chirality arises from either the presence of a chiral anion or the packing arrangement of the achiral constituents. Complexes with both oxygen and nitrogen donors are included in the achiral system, in order to control for any aspects related to the character of the M-L bond (e.g. covalency).

Prior to the scheduled beamtime, we omitted compound hexaaqua-nickel(II) sulfate from the study, it having been previously studied by the ID12 beamline scientists. The synthesis of nickel-doped bis(2,2':6',2''-terpyridyl)-manganese(II) diperchlorate hemihydrate did not give satisfactory crystals, and thus were replaced with $[Ni(terpy)2]_n[Cu_6(NCS)_2(CN)_6]_n$, which represent an achiral compound on a principal symmetry axis. Finally, the Δ enantiomer of [tris(9,10-phenantroline)-nickel(II) bis(triscatecholatoarsenate(V)) was also included in the study, being another chiral complex crystallizing on a principal symmetry axis.

In summary, the following crystals were prepared:

(**1**) tris(2,2'-Bipyridyl)-0,8zinc(II)-0,2nickel(II) bis(hexafluorophosphate)

(**2**) [tris(9,10-phenantroline)-nickel(II) bis(triscatecholatoarsenate(V))

(**3**) tris(2,2'-bipyridyl)-nickel(II) chloride (+)/(-)tartrate dodecahydrate

(**4**) $[Ni(terpy)2]_n[Cu_6(NCS)_2(CN)_6]_n$

(**5**) hexa-aqua-nickel(II) bis(camphor-10-sulfonate)

(**6**) bis(2,2':6',2''-terpyridyl)-nickel(II) bis(hexafluorophosphate)

We obtained the following spectra, all being performed at the Ni K-edge unless specified. It should be mentioned the listed spectra were obtained on numerous crystals, to ensure reproducibility. As the results have not yet been published, we will restrict our comments here to the experiments performed and some preliminary conclusions.

(**1**) XNCD spectra of Λ- and Δ-**1** in the orthoaxial orientation ($\theta = 90°$), and of one of the crystals (handedness unknown, to be determined by X-ray diffraction) in the axial position ($\theta = 0$) and at $\theta = 15°$, θ being the angle formed by the light wave vector and the *c* axis of the crystal. The enantiomorphic

crystals gave mirror-image spectra as expected, and the angular dependence was consistent with the expected function $3\cos^2\theta - 1$. The XNCD was also recorded at the Zn K-edge, but yielded a very weak and noisy response. XNLD (X-ray Natural Linear Dichroism) was recorded for one crystal in the orthoaxial orientation.

(**2**) XNCD for Δ-**2** at $\theta = 0°$ and 75°. The spectra showed a change in sign and intensity at the two angles, but due to the complex angular dependence of the monoclinic space group, calculations will have to be performed in order to quantitatively interpret the results. The XNCD at the As K-edge was also obtained. Finally XNLD was recorded for $\theta = 75°$.

(**3**) XNCD for both enantiomers of **3** were recorded with $\theta = 90°$ and $\theta = 45°$ with respect to the *b* crystallographic axis. At $\theta = 45°$ however, the spectra were close to zero, and not precisely mirror-images, due to slight misalignments in the crystals. The spectra with $\theta = 0°$ were also recorded, but due to alignment difficulties of the needle-shaped crystals, these results did not give the proper mirror-image spectra. On the axial-mounted crystals, XNCD was also obtained at $\theta = 45°$, giving satisfactory results. XNLD was also measured with $\theta = 0°$ and 90°.

(**4**) XNCD for one enantiomorphic crystal was obtained with $\theta = 90°$ with respect to the crystal *c* axis. Additional experiments could not be performed due to a lack of time.

(**5**) While these crystals were prepared, they were not measured due to a lack of time.

(**6**) XNCD was obtained on one crystal with $\theta = 0°$ and 45°. Unfortunately, these crystals were not stable to the beam (showing discoloration where the beam interacted with the crystal) or to the vacuum (showing a loss of crystallinity, likely due to loss of the acetone molecules of crystallization).

The first conclusion we can draw from the results is that the molecular chirality appears to play a very important role in the XNCD intensity. A second conclusion is that the local symmetry with respect to the crystal symmetry does not seem to have a strong impact on the XNCD intensity. These results will be now modeled using code under development by our team, which will certainly reveal more details about the role of symmetry in XNCD-active systems.