



**Experiment title:**

**X-RAY NATURAL CIRCULAR DICHROISM  
OF CHIRAL COMPLEXES ARTIFICIALLY ALIGNED  
IN ORIENTED LIQUID CRYSTALS**

**Experiment  
number:  
HE-330**

**Beamline:  
ID12-A**

**Date of experiment:** 1) from: May 15<sup>th</sup> 98 to May 17<sup>th</sup> 98  
2) from: June 05<sup>th</sup> 98 to June 06<sup>th</sup> 98

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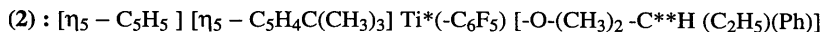
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## **I. WHY DO WE NEED TO ORIENT CHIRAL SPECIES IN ALIGNED LIQUID CRYSTALS ?**

We have produced recently the very first experimental evidence of X-ray Natural Circular Dichroism (XNCD) in a gyrotropic single crystal **1-3**. The origin of this effect was assigned to the Electric Dipole - Electric Quadrupole (E1 .E2) interference terms which contribute to the rank-2 pseudo deviator part of the Optical Activity tensor. There is, unfortunately, a dramatic limitation regarding possible extensions of XNCD to molecular systems in Chemistry or Biochemistry: since no pseudoscalar E1.M1 contribution can be detected in deep core level spectroscopies, the optical activity tensor is traceless in the X-ray range with the practical consequence that no XNCD can be detected in systems that have no orientational order such as solutions or powdered samples. This is because the Wigner rotation matrices associated with E1 and E2 are orthogonal. In order to circumvent this difficulty for systems for which no single crystal is available, we suggested a long time ago that a possible strategy was to dissolve the sample in a liquid crystal at a temperature slightly above the clearing point of a liquid crystal and then to cool the solution down to the nematic phase which can be most easily aligned in a strong magnetic field. Unfortunately, all our earlier attempts to exploit this technique had failed for several reasons: the poor solubility of the solute made such experiments too difficult in the transmission mode, the homogeneity of the magnetic field distribution had not been well enough controlled inside the fluorescence cell, the high heat load of our undulator beam was destroying locally the orientation order of the liquid crystal phase, the cells were leaking under vacuum etc... Having invested much time and effort in looking for the appropriate technical solutions, we are glad to report below on the very first successful experiment which is unambiguously establishing the feasibility of this very promising technique.

## II. RESULTS

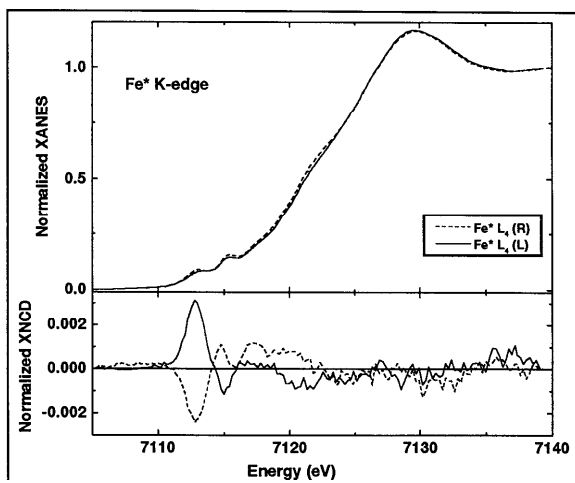
For our project HE-330, two families of *diastereoisomers* have been synthesized, resolved and purified at the university of Dijon: **(1)** :  $[\eta_5 - C_5H_5] Fe^*(-I)(-CO) [-P(Ph)_2(-N(CH_3)-C^*H(CH_3)(Ph))]$



We decided to concentrate our efforts on **(1)** for which the optical asymmetry of the metal is obvious<sup>1</sup>, associated with the tetrahedral coordination of iron bound to four different ligands: 1 Iodine, 1 Phosphorus of a substituted phosphine, 1 Carbon of a carbonyl group, 5 equivalent carbons of a  $\pi$ -bound cyclopentadienyl ring. This complex has a strong CD at optical wavelengths. The diamagnetic complex **(1)** was thus dissolved under anaerobic conditions in a thermotropic liquid crystal (Merck ZLI-4814; clearing temperature: 67°C). The clear solution was injected in a high vacuum fluorescence cell (at ca. 60°C) and the nematic phase was aligned in a high magnetic field (5T) oriented in the direction of the incident X-ray beam. XNCD spectra were recorded in the fluorescence mode in a supercooled, low temperature smectic phase. Due to the very low concentration of iron absorbing centers in solution (ca. 1000 ppm in g/g), and due to the small intensity of the XNCD signal, we had to reverse the circular polarization of the source for each energy of the scan. The XANES spectra of the two enantiomeric species and the corresponding XNCD spectra are reproduced in Fig. 1. The XNCD signal clearly reaches its maximum intensity (0.3%) for a pre-edge structure that is often suspected to be associated with electric quadrupole transitions. As expected, the two enantiomers have opposite signs for XNCD. The XNCD signal does not extend very far in energy compared to the XANES.

**Fig. 1a:** Xanes spectra of the two enantiomeric solutions (upper traces) ;

**Fig. 1b:** XNCD spectra of the two enantiomeric solutions (lower traces);



Refined analyses of this first experimental result, including *ab initio* simulations are in progress. We are facing, however, a major difficulty which is that the *exact* orientation of the complex in the smectic liquid crystal phase is unknown. From a parallel EXAFS study, we suspect that the substituted phosphine chain is aligned along the magnetic field but we cannot extract any accurate order parameter which should be better evaluated from NMR. Note that the two enantiomers may not be oriented exactly in the same way. Taking into account the rather small orientational order parameter ( $\leq 20\%$ ), one may anticipate that the XNCD signal should be quite large for a single crystal.

## References

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- 2 J. Goulon, F. Sette, C. Moise, A. Fontaine, D. Perey, P. Rudolf, F. Baudelet, Jpn J. of Appl. Phys., 32, (1993), 284-289
- 3 C. Goulon-Ginet, V. Gotte, A. Rogalev, J. Goulon, D. Perey, C. Moise, *manuscript in preparation*