



	Experiment title: ORBITAL MAGNETISM IN METALLOPORPHYRINS	Experiment number: HE-2390
Beamline: ID-12	Date of experiment: from: 02-MAY-2007 to: 08-MAY-2007	Date of report: 03-MAR-2008
Shifts: 18	Local contact(s): A. ROGALEV and F. WILHELM	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): <i>José GOULON^{1*}, Andrei ROGALEV^{1*}, Fabrice WILHELM^{1*}, Chantal GOULON-GINET^{1,2*}, Claude GROS³, Jean-Michel BARBE³ and Roger GUILARD³</i> ¹ European Synchrotron Radiation Facility (ESRF), B.P. 220, F-38043 Grenoble Cedex ² Université Joseph Fourier, Faculté de Pharmacie, Domaine de la Merci, F-38700, La Tronche ³ Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB), UMR CNRS 5260, Groupe LIMRES, 9 Avenue Alain Savary, BP 47870, F-21078 Dijon Cedex		

1. IS XMCD DETECTABLE IN PARAMAGNETIC METALLOPORPHYRINS ?

Metalloporphyrins appear in a wide variety of fundamental questions at issue in modern chemistry¹ and it is highly desirable to have a deeper insight into the electronic & magnetic structures of these complexes. Whereas EXAFS and XANES are perceived now as routine tools by chemists interested in metalloporphyrins^{1a}, this is not true regarding XMCD for a variety of reasons: (i) The XMCD signal vanishes at the K-edges of 3d transition metals whenever there is no *orbital* magnetization of the final states *via* spin orbit mixing with the magnetic ground state; (ii) XMCD studies on paramagnetic compounds require very low temperatures ($T < 20\text{K}$) and high magnetic fields ($B > 5\text{T}$) while several metalloporphyrins often order *antiferromagnetically* under such conditions; (iii) K-edge XMCD measurements remain extremely time-consuming on dilute paramagnetic systems and can be subject to artefacts due to radiation damage over long data acquisitions. While measurements become a lot easier at the L-edges of 4d-5d transition metals or rare earths, porphyrin chemistry of those elements is much less developed¹.

2. ESTABLISHED RESULTS

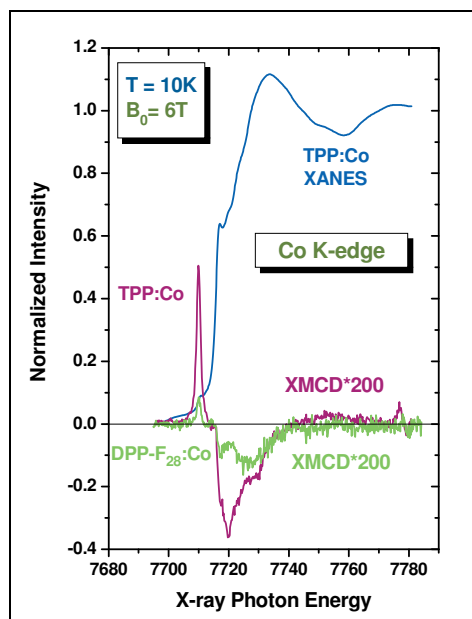
2.1. XMCD spectra of Vanadium (IV) porphyrins at the K-edge of Vanadium (d_1)

With an effective moment of *ca.* $1.73 \mu_B$, vanadyl porphyrins (C_{4v}) exhibit strong EPR lines with a characteristic hyperfine octet ($I = 7/2$). The rather isotropic spectroscopic splitting factors ($\Delta g^2 = g_{\parallel}^2 - g_{\perp}^2 = -0.098$) suggest that the orbital moment is heavily quenched. Nevertheless, we succeeded in measuring a very small XMCD signal ($1.2 \cdot 10^{-4}$) at the V K-edge of OEP:V=O ($T = 10\text{K}$; $B_0 = 6\text{T}$): this small signal can be assigned to a very weak Van Vleck paramagnetism.

In *trans*-dibromo-vanadium (IV) porphyrin (D_{4h}), *i.e.* OEP:V(Br)₂, the ground state (2E_g) was predicted to be orbitally degenerate²: spin orbit coupling may then result in a short relaxation time T_{1e} explaining why this compound is EPR silent. If spin orbit coupling was affecting as well the final states, one would expect the XMCD signal to be enhanced as compared to the case of OEPV=O. This was *not supported* by our

experiments. Note that, within the electric dipole (E1) selection rules, XMCD will probe only the paramagnetism of $\{a_{2u}, e_u\}$ final states but not of the e_g ground states that should be probed in EPR.

2.2. XMCD of Cobalt (II) porphyrins at the K-edge of Cobalt (d_7)



In planar, low spin Co (II) porphyrins (e.g. TPP:Co), the ground state is postulated^{1b,3,4} to be a Kramers doublet 2A_1 with a close lying doubly degenerated excited state $\{e\}$. A large g -anisotropy ($\Delta g^2 \approx -7.80$) was reported⁴ for the EPR octet ($l = 7/2$). This is supporting the assumption that there might be a significant (partially unquenched) **orbital moment** in the ground state, whereas magneto-optical sum rules imply that spin orbit coupling should also play a significant role in the excited final states. This was supported by the detection of a significant XMCD signal at the Co K-edge of TPP:Co. In particular, a sharp XMCD signal was observed in the pre-edge region where electric quadrupole transitions (E2) are expected to exhibit the largest contribution involving Co (3d) densities of states. A substantial decrease of the XMCD signal was observed with the complex DPP-F₂₈:Co. Here, perfluorinated substituents tend to attract the electrons and may induce a quite sensible delocalization of the orbital magnetic moment whereas the non-planarity of the porphyrin macrocycle is enhanced by such bulky substituents.

2.3. XMCD a Manganese (III) porphyrin at the K-edge of Manganese (d_4)

It is well documented that high spin Mn (III) porphyrin complexes are *non-Kramers* paramagnets ($S = 2$) with a rather large *zero field splitting* ($D \approx -2.3 \text{ cm}^{-1}$) which makes them EPR-silent unless EPR experiments are carried at high pumping frequency (226-544 GHz). Nevertheless, a significant XMCD signal was again detected at the Mn K-edge for TPP:Mn-Cl: this results confirms the reality of the existence of unquenched orbital magnetization components at the Mn site. Whereas nice XANES spectra could be recorded at the Cl K-edge, XMCD experiments were unfortunately hopeless at the Cl K-edge because the Si(111) double crystal monochromator operated at Bragg angles near 45° Bragg acted as a powerful linear polarizer.

2. FURTHER WORK TO BE COMPLETED

Unfortunately, the beamtime required to record fully reliable XMCD spectra turned out to be much longer than anticipated because time-consuming data acquisition procedures had to be used in order to minimize radiation damages. No time was left free for XMCD studies of species, e.g. pentacoordinated Mn (II) complexes, involved as precursors of 1-D molecular magnets. Moreover, unexpected difficulties experienced in Dijon in the synthesis of 5d homo- & hetero-bimetallic complexes, e.g. Por:[Os=Os]:Por or Por [W=Os]:Por, led us to cancel that part of the project. Unfortunately, given that the scientific priorities of the groups involved in this collaboration have evolved, it is far from certain that a re-activation of this project can be envisaged in a near future. In the short term, we wish to refine the quantitative analyses of the XMCD spectra already collected at the K-edges of 3d metals. Note that a fully relativistic PY LMTO-LSDA simulation of a porphyrin complex looks like a *tour de force* because of the huge number of atoms in the primitive cell. This is why we may have to keep going on with less demanding multiple scattering methods.

REFERENCES

- ¹ K. Kadish, K.M. Smith and R. Guilard, Eds., *The Porphyrin Handbook*, Vol. **1-10**, (2000); Vol. **11-20** (2006)
 - 1a) J. Goulon, C. Goulon-Ginet and V. Gotte, *X-ray Absorption Spectroscopy Applied to Porphyrin Chemistry*, Vol. **7**, chapt. 49, pp.79-166 (2000).
 - 1b) F. Ann Walker, *Proton NMR and ESR of Paramagnetic Metalloporphyrins*, Vol. **5**, chapt. 36, pp. 81-183 (2000).
- ² P. Richard, J.L. Poncet, J.M. Barbe, R. Guilard, J. Goulon, D. Rinaldi, A. Cartier, P. Tola, *J. Chem. Soc. Dalton Trans.* 1451 (1982).
- ³ W.C. Lin, *ESR & Electronic Structure of Metalloporphyrins* in: *The Porphyrins*, D. Dolphin Ed., Vol. **IV**, chapt. **7**, 355 (1979).
- ⁴ F. Ann Walker, *J. Am. Chem. Soc.* **92**, 4235-44 (1970). \