ESRF	**Experiment title:** **First experimental evidences of a magnetic polarisation of the *2p* nitrogen orbitals in organic molecules**	**Experiment number:** **HE1228**
Beam line **ID08**	**Date of experiment**: **from: 03/06/2002 to: 10/06/2002**	25/08/2002
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We report on XMCD experiments on two series of organic molecules:

1- Molecule based magnets: $Cs^{I}[Ni^{II}Cr^{III}(CN)_6]$

We are engaged in the synthesis of new molecule-based magnets of formula $Cs^{I}[A^{II}Cr^{III}(CN)_6]$ (A^{II}=transition metal), with a three-dimensional Prussian-Blue structure. The divalent A^{II} and trivalent Cr^{III} ions are coupled through the cyano (CN) bridges. By varying the nature and the stoechiometry of the A^{II} cation we can control the macroscopic magnetic properties as the nature of the exchange interaction between the cations or the T_C temperature. Since no single crystals are available for this series, we are measuring the local magnetic properties by XMCD to get insight on the magnetic properties and coupling.

For the $Cs^{I}[Ni^{II}Cr^{III}(CN)_6]$ compound (T_C = 90K), we have recorded the XMCD signals at the $L_{2,3}$ edges of chromium nickel transition metal ions (Figure 1) and at the nitrogen K edge, at T=40K and H=±2T (Figure 2). We have checked that the samples are stable under the beam of ID08 and that charging effects could be eliminated by appropriate sample preparation.

We have analysed the $L_{2,3}$ edges of the transition elements and the corresponding dichroic signals through Ligand Field Multiplet calculations. In the calculations, hybridisation has to be taken into account due to the large covalence of the CN bond.

Since the cyano bridge plays such an important role in this series of compounds, the need for measuring the local magnetic properties of nitrogen is obvious. At the nitrogen K edge, a small (≈1%) XMCD signal has been measured. It is a very structured signal where feature A could be attributed to hybridisation with the *3d* transition ion orbitals and B feature is the π^* antibonding molecular orbital of the cyano bridge. Though it is well known that XMCD at K edges is not a direct measure of local spin polarisation, it has nevertheless been shown that it is related to the magnetic moment carried by the p orbitals and to the spin polarisation of the magnetic neighbours. Quantitative information can only be obtained by *ab initio* calculations. Such calculations developed for a semi relativistic Hamiltonian are in progress.

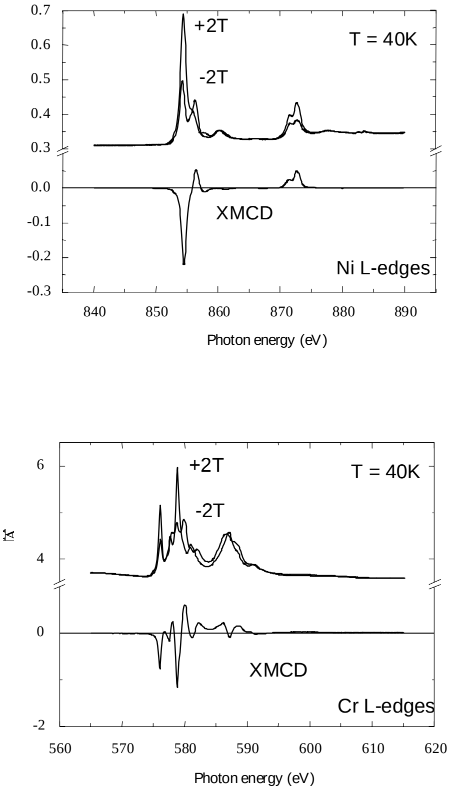


Figure 1. *XAS and XMCD at the Ni- and Cr-$L_{2,3}$ edges in the $Cs^{I}[Ni^{II}Cr^{III}(CN)_6]$ compound, at T=40K and H=2T*

2- Langmuir-Blodgett films of an organic paramagnet

a) *Imino-nitroxide molecule*: The study[1] reported here has been performed on a diradical from the imino-nitroxide (IN) family. The molecule has a rodlike structure with the two IN groups at the end of a phenylene-ethynylene core. Electron paramagnetic resonance (EPR) measurements have confirmed that each molecule bears a $2\mu_B$ moment as expected. The pure material crystallises in the P21/c space group and previous EPR measurements revealed a weak antiferromagnetic coupling of the two spins.

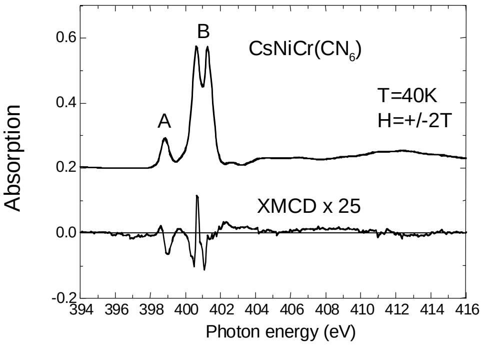


Figure 2 *XAS and XMCD at the N-K edge in $Cs^I[Ni^{II}Cr^{III}(CN)_6]$ compound, at T=40K and H=2T*

On figure 3, the curve (a) gives a typical N-*K* absorption edge, while the curve (b) corresponds to the dichroism spectrum. The dichroism is deduced from the point-to-point difference of two absorption spectra taken either at two different light polarizations or two different magnetic field directions. The curve (b) is therefore an average of 4 dichroism spectra obtained from eight successive energy scans. The multiplet feature around 402 eV is a parasitic signal from molecular nitrogen adsorbed on the surface of the sample. The clear observation of a dichroism signal (≈5%) demonstrates that the nitrogen atoms carry a significant magnetic moment.

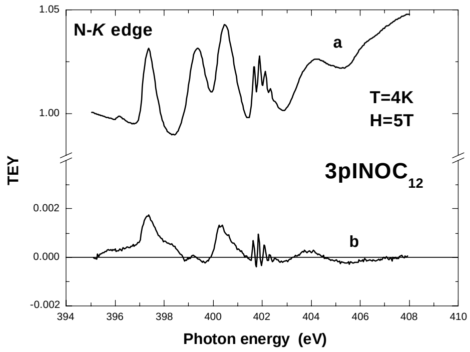
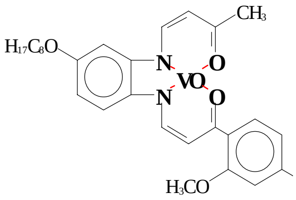


Figure 3. *N-K edge and XMCD in the $3pINOC_{12}$ molecule, at T=4K and H=5T*

b) *Vanadyl VO^{2+} complex*: Our study has been performed on a vanadyl *bis*-enaminoketone complex in which the V(IV) atom is a chiral center[2] contrary to other vanadium(IV) complexes whose structure is symmetrical. Figure 4 presents the N-*K* edge and the corresponding dichroism signal, at T=4K and H=6.5T. As in the previous case, the absorption spectrum reveals the presence of N_2 molecules at the surface of the sample. But as the structures of this parasitic contribution is well localised around 402 eV, the intrinsic absorption of the N atoms, neighbours of the VO^{2+} ions, shows unambiguously a magnetic signature around the main structure of the *K* edge. This dichroic effect is be due to the sole spin polarisation of the V-*3d* orbitals (paramagnetic state).



To the best of our knowing this is the first observation of such an effect on a purely organic material. These results raise the question of **the existence of a direct correlation between the dichroic signal at the N-*K* edge and the *p* spin densities**. To support this assumption we need more experiences on molecules with different N environments and a strong effort of simulations for a theoretical interpretation of dichroic signals at the *K* edge of nitrogen.

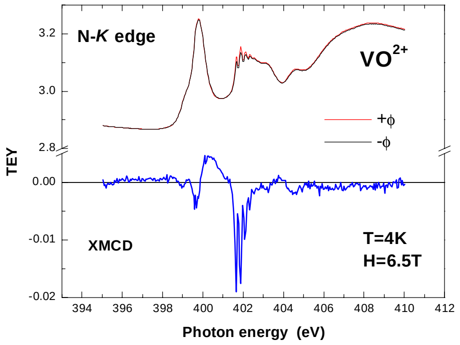


Figure 4. *N-K* edge *and XMCD in vanadyl VO^{2+} complex, at T=4K and H=6.5T*

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[1] Gallani *et al.*, Langmuir, to be published (2002)

[2] Gallani *et al.* Highlights ELETTRA (2002)