ESRF	**Experiment title:** Investigate the magnetic structure of copper(II)-based organic/inorganic coordination polymers hybrid single crystals	**Experiment number**: MA-5241
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Report:

The perovskite-like organic-inorganic hybrids systems have demonstrated to exhibit a plethora of important technological features like the modulation/tuning via coordination chemistry methodologies of their properties. In this context, we have tried to solve the electronic and magnetic properties of hybrid copper based materials, checking the presence of ferromagnetism (FM) in the 1D $\{Cu\text{-}(\mu\text{-}X)_2\}_n$ linear chains along the cristallogaphy *a*-axis (see Figure 1a) and/or weak FM between the planes and deepening the presence of a frustrated antiferromagnetic state (AFM) inside the plane. For this reason, we have grown 1,2,5-benzothiadole/$CuCl_2$ ((btd)/$CuCl_2$), 1,2,5-benzothiadole/$CuBr_2$ ((btd)/$CuBr_2$) and 1,2,5-benzoselenadizole/$CuCl_2$ ((bSed)/$CuCl_2$) isomorphic compounds with monoclinic structure ($P2_1/m$) in the form of single crystals[1] to put in correlation the magnetic properties with some chemical substitution. In this structure each Cu^{2+} atom is octahedrally coordinated to four halogen atoms and two molecules with Jahn-Teller distortions.

In this experiment we used X-ray absorption spectroscopy at the ID32 beamline of the ESRF, equipped with a 9Tmagnet, by using simultaneously Total Electron Yield (TEY) and Fluorescence Yiedl (FY) detection methods. x-ray magnetic dichroism (XMCD), x-ray magnetic linear dichroism (XMLD) and x-ray linear

Figure 1b

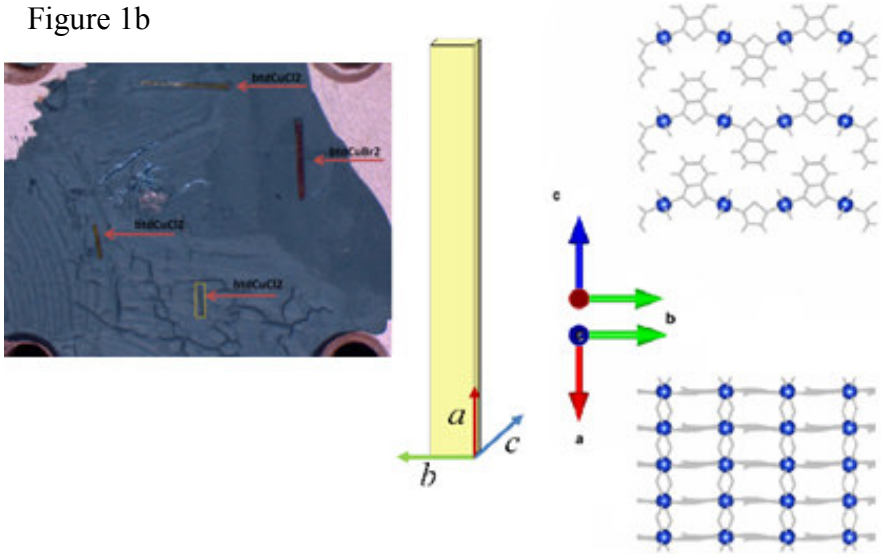

Figure 1a

dichroism (XLD) at the Cu $L_{2,3}$ edge on these three samples were performed.
Up to 16 Cu L-edge XAS spectra, acquired with right and left helicity or vertical and horizontal polarization, have been averaged to eliminate any source of systematic error and to reduce the noise level. We show data acquired at low temperatures (5K), performed in grazing incidence (GI) and normal incidence (NI) conditions.
To have a good electronic connection for TEY detection we have glued the samples using colloidal graphite, on copper sample holder used to have better thermal coupling going at low temperature, see the images in Figure 1a.
In Figure 2, we show the Cu-L edge XMCD spectra taken on (btd)$CuCl_2$ (Figure 2a) and (btd)$CuBr_2$ (Figure 2b) samples, in both cases we observe a dichroic signal, not saturate at high field, but increased until 5 Tesla for both compounds.
Performing XMLD on both compounds we observe that the spectra are different (Figure 3a and 3b, from $3d_z^2$ to a combination of $3d_x^2$ and $3d_y^2$) between the two samples characterized by different halogen atoms (from Cl to Br). In particular, as shown in Figure 3a, on the (btd)$CuCl_2$ sample at 5 Tesla, a change of the XLD spectra is observed. Maybe this could be due to the presence of the AFM order in the plane.
Performing XMCD measurements on (btd)$CuCl_2$ in GI configuration, when the field is along *b*-axis (exploring the$\{Cu\text{-}N\text{-}S\text{-}N\}_n$ chains) no dichroic signal is observed (see Figure 3b) at 5Tesla, coherently with the magnetic data reported in literature on powders that propose a 1D-AFM model to describe the measurements of susceptibility, where the main exchange interaction was related to the $\{Cu\text{-}N\text{-}S\text{-}N\}_n$ chains.[2] We suppose that for the (btd)$CuCl_2$ it is playing an important role the presence of an AFM order, due to a canting of the spin on Cu atoms.

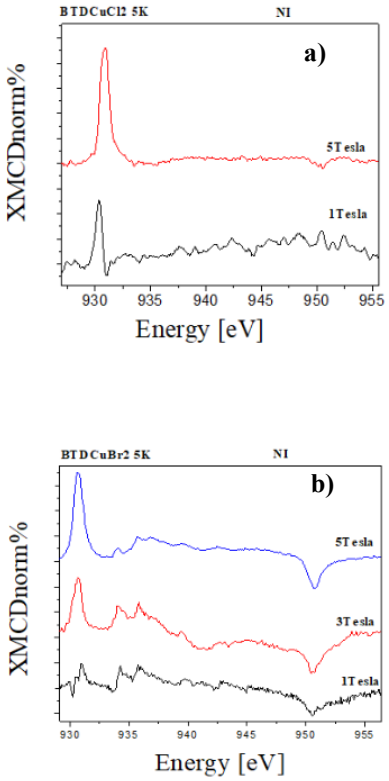

Figure 2. TEY XMCD normalized spectra in NI configuration at 5 K on (a) (btd)$CuCl_2$ and (b) (btd)$CuBr_2$

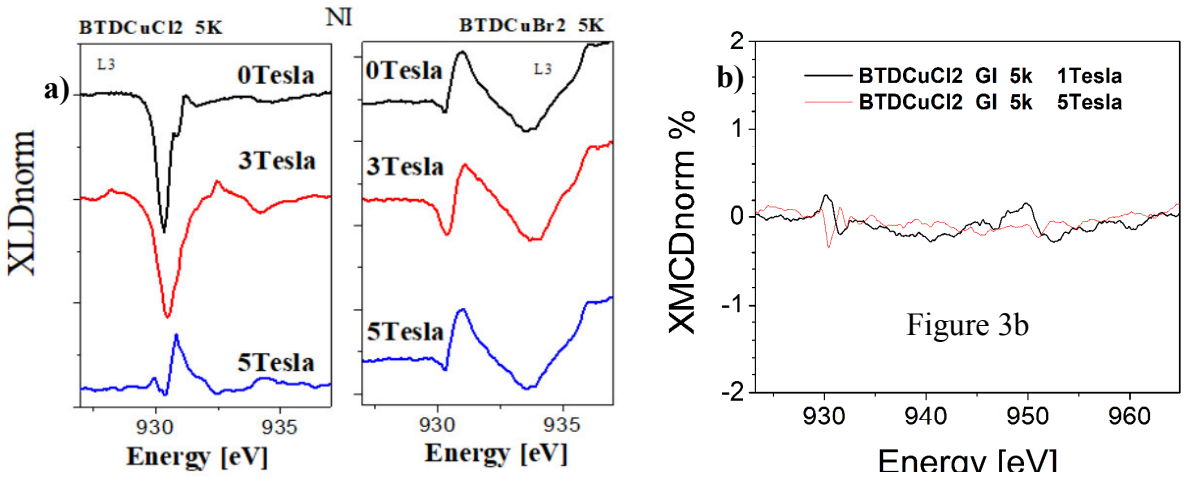

Figure 3. (a)XLD spectra normalized performed in TEY configuration as function of the magnetic field on (btd)$CuCl_2$ (left pannel) and on (btd)$CuBr_2$ (rigth pannel). (b) XMCD spectra in GI configuration on (btd)$CuCl_2$

If from these preliminary results is clear that the halogen atom is influencing the orbital order of the compound, on the other hand the change of the organic ligand is crucial for a different magnetic behaviour along the *b*-axis, as shown in Figure 4. Here, contrary from what was observed in Figure 3b, the XMCD signal is not zero, but increase with the magnetic field even if the saturation is reached at 3 Tesla.
Part of the results attended from this experiment show us the possibility to have a frustrated AFM order clear in (btd)$CuCl_2$, but to be investigated deeply in (bSed)$CuCl_2$. However, the magnetic response as function of the magnetic field cannot be attributed directly to a ferromagnetic order, if we will not proceed to improve the measurements increasing the magnetic field and performing measurements as function of the temperature, to observe as shown in literature for the $CuCl_2$ parent compound[3,4] a transition temperature. Moreover, it will be

necessary to have a clearer picture of the system investigated to perform measurements with the magnetic field along the $\{Cu\text{-}(\mu\text{-}X)_2\}_n$ linear chains (*a*-axis), to better demonstrate the helicity spin order that we expect. Unfortunately, the experiment was not so easy due to the small size of the sample and the difficulties in the alignment did not permit to perform all the measurements.

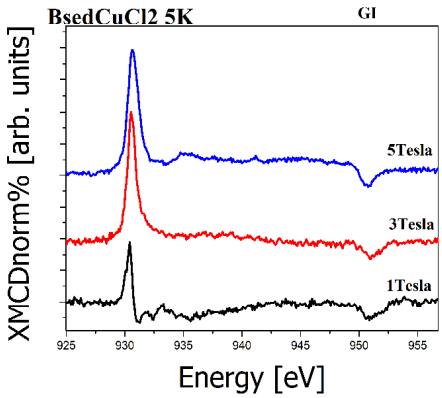

Figure 4. XMCD normalized spectra in GI configuration performed on (bsed)$CuCl_2$

Conclusions: we observe that in (btd)$CuCl_2$ the XMCD signal is present along the NI configuration and disappear in GI when the field is applied perpendicular to the molecular ligand chain (*b*-axis in Figure 1), on the contrary when we change the organic ligand the XMCD signal is observed in GI configuration. This is demonstrating that the organic ligand is playing a role in the magnetic configuration of these compounds. The presence of an AFM feature is observed in (btd)$CuCl_2$ performing XMLD, however these results are not conclusive; to have a clear understanding of the magnetic properties it will be necessary to perform XMCD measurements as function of the temperature too.

[1] E. Parisi, A. Carella, F. Borbone, F. Chiarella, F.Gentile, and R.Centore, Effect of chalcogen bond on the packing and coordination geometry in hybrid organic-inorganic Cu(II) networks. CrystEngComm, 2022,**24**, 2884-2890.
2 G. S. Papaefstathiou, A. Tsohos, C. P. Raptopoulou, A. Terzis, V. Psycharis, D. Gatteschi, and S. P. Perlepes Crystal Growth & Design, 1, 191-194 (2001).
3 M. G. Banks, R. K. Kremer, C. Hoch, A. Simon, B. Ouladdiaf, J.-M. Broto, H. Rakoto, C. Lee, and M.-H. Whangbo Phys. Rev. B 80, 024404 (2009).
4 L. Zhao, T.-L. Hung, Ch.-Ch. Li, Y.-Y. Chen, M.-K. Wu, R. K. Kremer, M. G. Banks, A. Simon, M.-H. Whangbo, C. Lee, J. S. Kim, I. Kim, and K. H. Kim Adv. Mater. 24, 2469–2473 (2012).