



	Experiment title: Photomagnetic octacyanotungstates	Experiment number: CH-6239
Beamline: ID12	Date of experiment: from: 8/03/2022 to: 15/03/2022	Date of report: 13/09/2022 <i>Received at ESRF:</i>
Shifts: 18	Local contact(s): Andrei Rogalev	
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Report:

Scientific background

This proposal was devoted to the study of the local magnetic properties of photomagnetic octacyanometalates. Over the past decade there has been considerable interest in the development of tunable molecule-based materials that exhibit bistability in their physical properties as a function of external stimuli. Octacyanometalates, in particular octacyanomolybdate and octacyanotungstate exhibit these bistable properties. At low temperatures, they are diamagnetic and upon light irradiation in the visible range they become paramagnetic. XAS and XMCD studies done at ID12-ESRF on some of the $[\text{Mo}^{\text{IV}}(\text{CN})_8]^{4-}$ and $[\text{Mo}^{\text{III}}(\text{CN})_7]^{3-}$ compounds in the past (CH-5712, manuscript under preparation) have proved to be useful in observing the photomagnetic effects. In this proposal, we wanted to study a similar class of compounds containing W instead of Mo ions.

Experimental details

The selected $(\text{cat})_x[\text{M}(\text{CN})_y]^{n+}$ compounds are air sensitive and are surrounded by solvent molecules, which have a strong influence on the photomagnetic properties of the compounds. The compounds had to be protected from air and from desolvation in ultra-high vacuum conditions. Thus the samples were prepared in a glove box at ID12 on the sample holder containing solids or solutions and sealed by a kapton film or a polyethylene film. The kapton film allows the penetration by X-rays and by the different light sources (infrared LED and white lamp) used for photoexcitation. For the solid samples, we encountered several difficulties due to diffraction peaks appearing in the XAS spectra. That is why we measured for all the compounds solid and solution XAS spectra at room temperature. The specific set-up for light irradiation (8 Tesla solenoid with in-situ optical irradiation) has been used to measure the photo-excited state in our systems. We used different light sources (blue and green LED). We were able to measure **four samples**: three mononuclear compounds $\text{Na}_3[\text{W}^{\text{V}}(\text{CN})_8]$, $\text{K}_4[\text{W}^{\text{IV}}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$ and $(\text{K}@\text{cryptand})_3[\text{W}^{\text{IV}}(\text{CN})_7] \cdot n\text{MeCN}$ complexes used as references and the $\{[\text{Mn}^{\text{II}}_2(\text{pyridazine})][\text{W}^{\text{IV}}(\text{CN})_8]\}_n$ coordination polymer.

We measured:

- 1) the XANES at room temperature for the reference complexes at W L_{2,3} edges (figure 1) for solutions.
- 2) the XANES at room temperature for the reference complexes at W L_{2,3} edges (figure 2) for solids.
- 3) the XANES at 300 and at 2 K for the coordination polymer at Mn K edges and W L_{2,3} edges, before photoexcitation.
- 4) the XANES at 3 K at Mn K and W L edges after 18 hours of blue and green light excitation
- 5) the XMCD at 3 K at W L edges after 18 hours green light excitation.

Results

Figure 1 and 2 show the XAS of the reference compound $K_4[W^{IV}(CN)_8] \cdot 2H_2O$ which is similar in solid state and in solution.

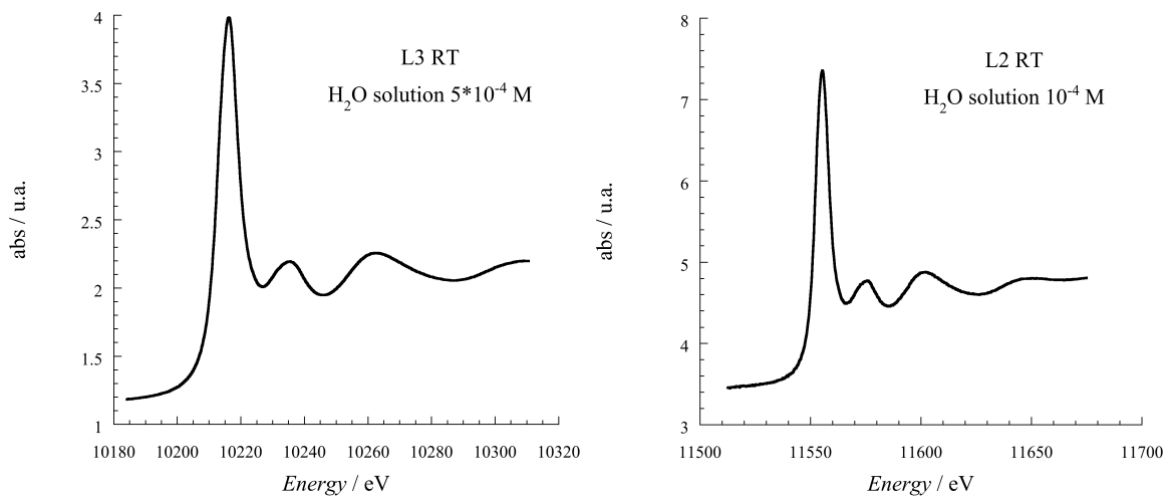


Figure 1: XANES at W L₃ (left) and L₂ edge (right) at 300 K (green) for the aqueous solutions ($C = 10^{-4}$ M) of $K_4[W^{IV}(CN)_8] \cdot 2H_2O$

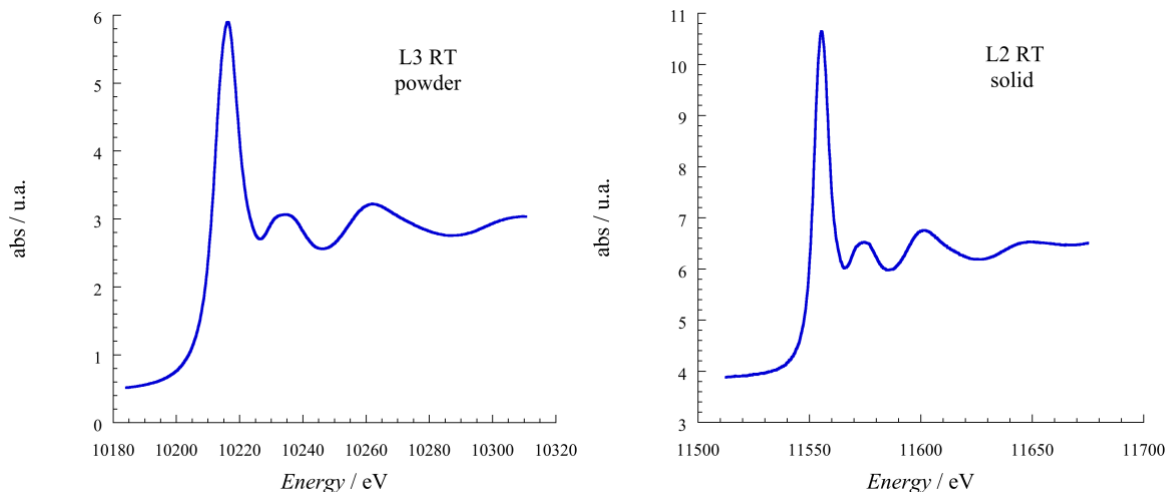


Figure 2: XANES at W L₃ (left) and L₂ edge (right) at 300 K (green) for the solid $K_4[W^{IV}(CN)_8] \cdot 2H_2O$

Figure 3 compares the XAS spectra of the three mononuclear compounds at room temperature : $Na_3[W^V(CN)_8]$, $K_4[W^{IV}(CN)_8] \cdot 2H_2O$ and $(K@cryptand)_3[W^{IV}(CN)_7] \cdot nMeCN$ in the solid state. The spectrum of $Na_3[W^V(CN)_8]$ (W^{5+} having a $5d^1$ electronic configuration) is less intense than the spectrum of $K_4[W^{IV}(CN)_8] \cdot 2H_2O$. This is not in agreement with the electronic configuration of the W metal ion in the two compounds (W^{4+} in $K_4[W^{IV}(CN)_8] \cdot 2H_2O$ with a $5d^2$ electronic configuration versus W^{5+} in $Na_3[W^V(CN)_8]$ with a $5d^1$ electronic configuration). We conclude that the spectrum of $Na_3[W^V(CN)_8]$ is wrong. This was

confirmed at the end of the experiment when we examined the sample under the microscope. We observed a black circle probably corresponding to the impact of the X-ray beam that damaged the compound. This suggests the X-ray sensitivity of the $\text{Na}_3[\text{W}^{\text{V}}(\text{CN})_8]$. On the opposite, the 2 other compounds show similar but not identical XAS spectra in agreement with the W in the same +4 oxidation state. The structural difference between $\text{K}_4[\text{W}^{\text{IV}}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$ and $(\text{K}@\text{cryptand})_3[\text{W}^{\text{IV}}(\text{CN})_7] \cdot n\text{MeCN}$ is the number of the CN groups around the metal center modifying the geometry around the metal center from a triangular dodecahedron to a pentagonal bipyramidal geometry, respectively. We will consider the XAS spectra of these two complexes as reference spectra.

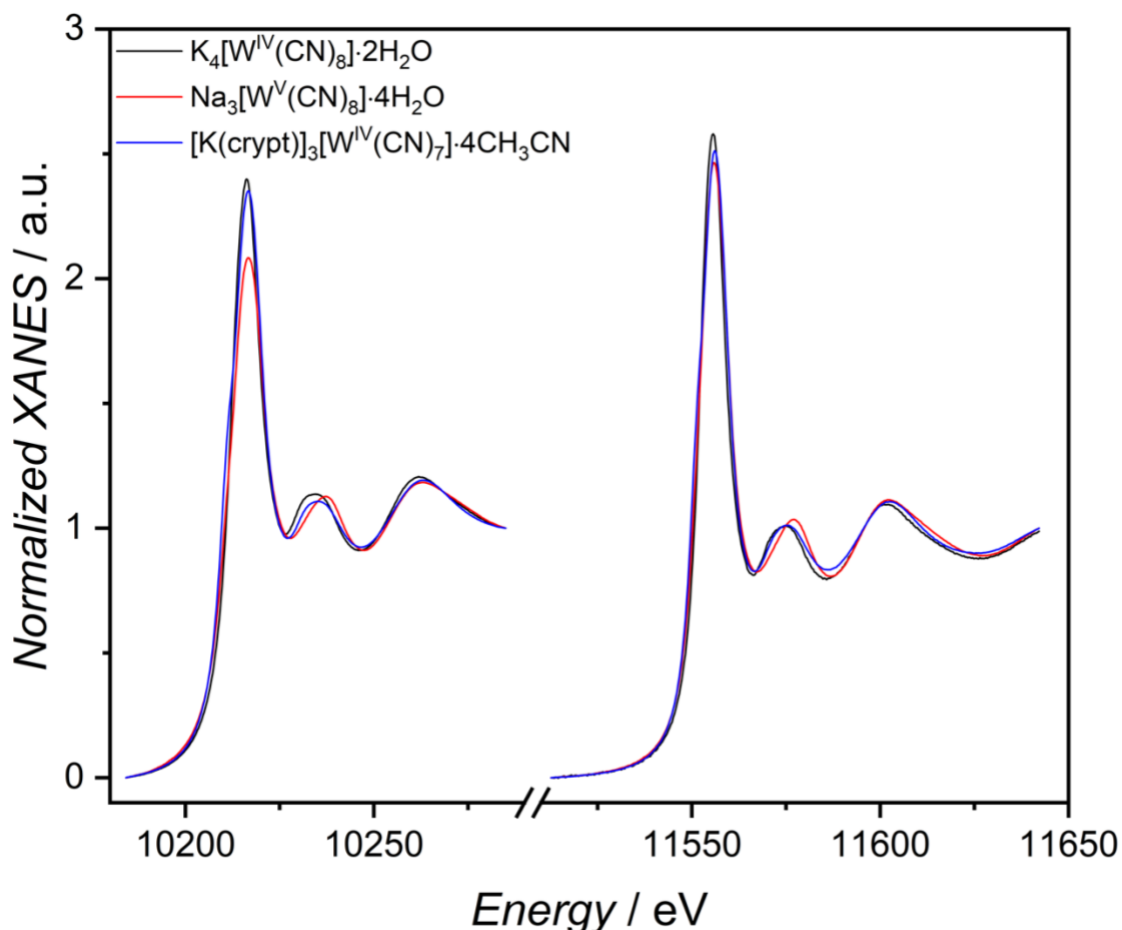


Figure 3: XANES at W L3 (left) and L2 edge (right) at 300 K for the solids of $\text{K}_4[\text{W}^{\text{IV}}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$ (dark), of $\text{Na}_3[\text{W}^{\text{V}}(\text{CN})_8]$ (red) and of $(\text{K}@\text{cryptand})_3[\text{W}^{\text{IV}}(\text{CN})_7] \cdot n\text{MeCN}$ (blue)

During the remaining time of this beamtime we were able to measure the XANES measurements for $\{[\text{Mn}^{\text{II}}_2(\text{pyridazine})][\text{W}^{\text{IV}}(\text{CN})_8]\}_n$ that use of the second harmonic of helical undulator with Al attenuators allows radiation damage of the samples to be avoided whereas the signal-to-noise ratio in the spectra is sufficiently good to record XMCD spectra at the L2,3-edges of W. We have also checked that the compound is stable in the condition of our experiment.

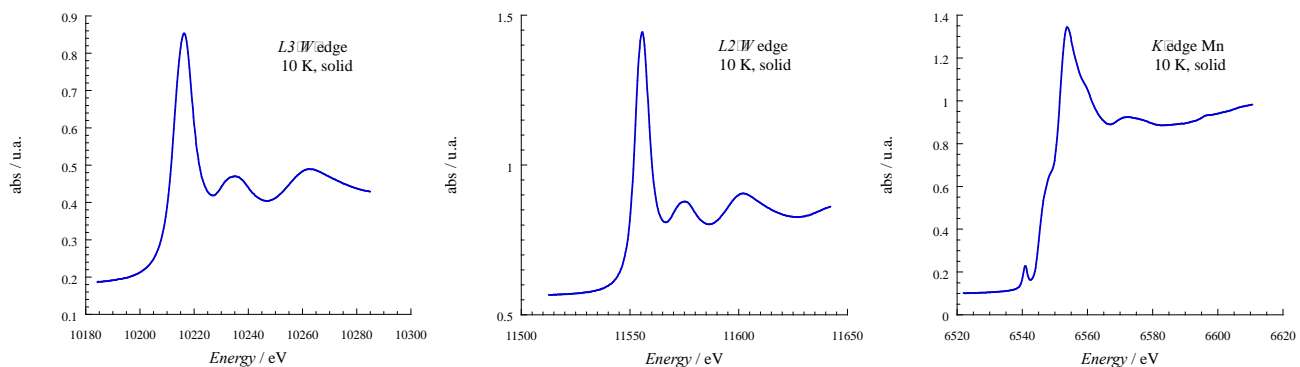


Figure 4: XANES at W L3 (left) and W L2 edges (middle) and K edge (right) at 10 K for the solid of $\{[Mn^{II}_2(pyridazine)][W^{IV}(CN)_8]\}_n$

These preliminary results prompt us to propose complete XAS/XMCD measurements for the photo-induced states of $\{[Mn^{II}_2(pyridazine)][W^{IV}(CN)_8]\}_n$ as well as three other Mn^{II} - $[W^{IV}(CN)_8]$ coordination polymers with confirmed photomagnetic behaviour by SQUID photomagnetic measurements: $\{[Mn^{II}(imH)]_2[W^{IV}(CN)_8]\}_n$, $\{Mn^{II}[Mn^{II}(H_2O)_2][W^{IV}(CN)_8]\}_n$ and $\{(NH_4)_2Mn^{II}_3[W^{IV}(CN)_8]_2\}_n$