

### XANES study of the (H<sub>3</sub>O)[Ni(cyclam)][Fe(CN)<sub>6</sub>]-5H<sub>2</sub>O dehydration process

W. Szmyt<sup>1\*</sup>, T. Strączek<sup>1</sup>, A. Czajka<sup>1</sup>, K. Gąska<sup>1</sup>,  
D. Zając<sup>1</sup>, J. Zukrowski<sup>1</sup>, Cz. Kapusta<sup>1</sup>,  
M. Reczyński<sup>2</sup>, B. Nowicka<sup>2</sup> and B. Sieklucka<sup>2</sup>

<sup>1</sup>AGH University of Science and Technology, Faculty of  
Physics and Applied Computer Science, Department of Solid  
State Physics, al. A. Mickiewicza 30, 30-059 Kraków, Poland  
<sup>2</sup>Faculty of Chemistry, Jagiellonian University, Ingardena 3,  
30-060 Krakow, Poland

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\*e-mail: Wojciech.Szmyt@fis.agh.edu.pl

Molecular magnets are a class of compounds which have recently attracted a great deal of interest owing to their potential usability in many fields of technology such as magnetoelectronics, spintronics or quantum information processing [1]. They can exhibit paramagnetic behaviour or, owing to spin-coupling, a long-range magnetic order at low temperatures can be achieved [2].

In this work we study a molecular magnet (H<sub>3</sub>O)[Ni(cyclam)][Fe(CN)<sub>6</sub>]-5H<sub>2</sub>O, (cyclam = 1,4,8,11-tetraazacyclotetradecane) containing iron and nickel ions alternating in a chain sequence, which makes it a one-dimensional (1-D) structured material. The molecule unit is depicted in Figure 1.

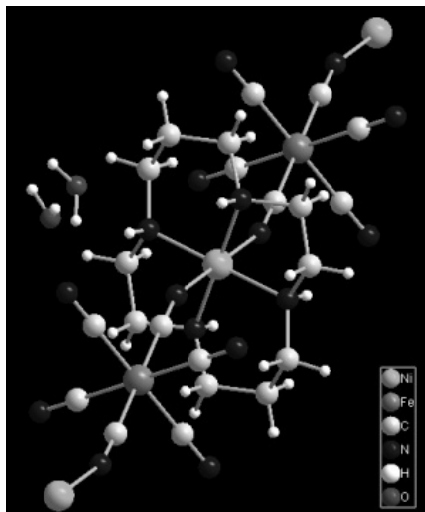


Figure 1. The illustration of the molecular structure – Fe-Ni molecular magnet with two H<sub>2</sub>O molecules located. Structure investigated by XRD.

For the materials studies magnetic measurements have been carried out.

The temperature dependence of magnetic susceptibility shows that down to 100 K the hydrated compound is a paramagnet and the dehydration

considerably changes the value of the effective magnetic moment. The measurements have also indicated that at low temperatures, below ~100 K, ferromagnetic correlations are possibly present, resulting in a significant increase in the magnetic susceptibility of the sample. The effect was much stronger in the case of dehydrated material and occurred already at a higher temperature than for the hydrated material. Measurements of magnetisation versus magnetic field have shown a metamagnetic transition occurring for the dehydrated sample at a field of 6 kOe.

The material has also been examined by <sup>57</sup>Fe Moessbauer spectroscopy. An example of the spectrum measured at 4.2 K for the dehydrated sample is shown in Figure 2.

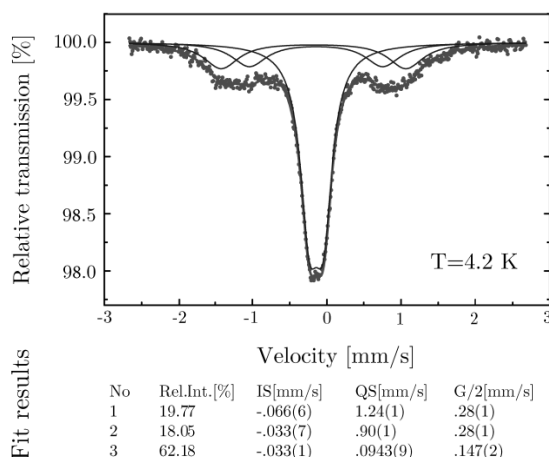


Figure 2. <sup>57</sup>Fe Mossbauer spectrum of the dehydrated sample at the temperature 4.2 K together with a best fit result, green line. Three doublets fitted are marked as blue lines. Below the graph there are results of fitting, i.e. relative intensities of the doublets, their isomer shift, IS, quadrupole splitting, QS and the linewidth values shown.

No magnetic splitting is observed and the spectrum consists of three quadrupole doublets. For the hydrated sample just one doublet is observed corresponding to the most intense one with the smallest splitting observed for the dehydrated sample. The effect indicates that for the dehydrated sample two additional different states of Fe ion, corresponding to a highly nonspherical distribution of electronic charge appear.

X-ray Absorption Spectroscopy (XAS) study has been carried out in the XANES range of the Fe and Ni L<sub>3</sub> and L<sub>2</sub>-edges. The measurements have been done in the Helmholtz-Zentrum Berlin at a bending magnet beamline of the synchrotron radiation storage ring BESSY II. The spectra were recorded in the total electron yield (TEY) and partial fluorescence yield (PFY) modes at room temperature. The TEY spectra are presented in Figure 3. The L<sub>2</sub> and L<sub>3</sub> absorption edges correspond respectively to electronic transitions from the 2p<sub>1/2</sub> and 2p<sub>3/2</sub> core orbitals to the 3d states above the Fermi level.

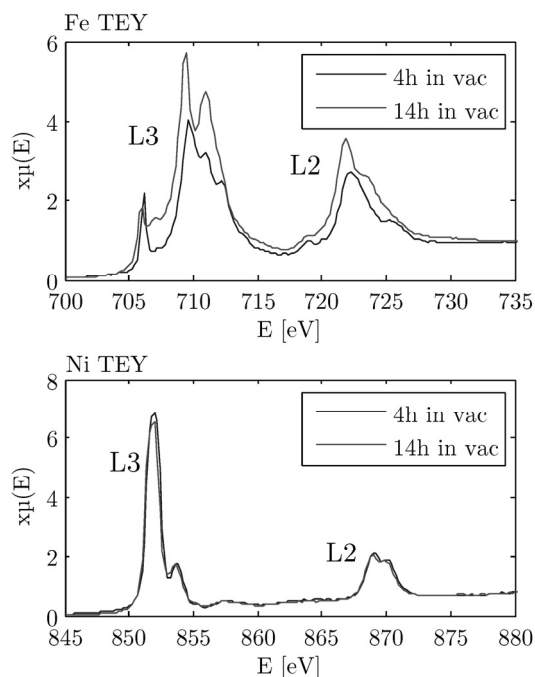


Figure 3. XANES spectra of the materials studied at the  $L_2$  and  $L_3$  edges of Fe and Ni in the TEY mode. Red line stands for dehydrated sample, blue line – for the hydrated one.

In the simulations of XANES spectra we have used the FEFF 8.4 XAS software and the IFEFFIT library-based software - ARTEMIS and ATHENA - to generate the sample and analyse the simulation results, respectively. Subsequent releasing of water molecules was realized by removing the two inequivalent molecules (**1** and **2**) in the unit cell. Four variants have been examined, i.e. both molecules present, molecule **1** present, molecule **2** present, none of them present. The resulting spectra are shown in Figure 4.

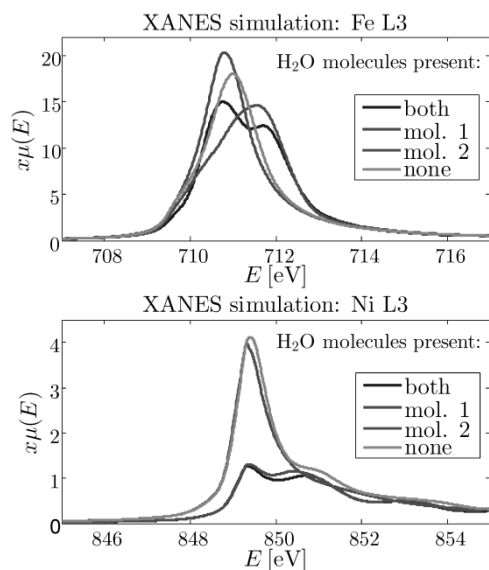


Figure 4. Simulated XANES spectra of  $(\text{H}_3\text{O})[\text{Ni}(\text{cyclam})][\text{Fe}(\text{CN})_6]\cdot 5\text{H}_2\text{O}$ , at the  $L_3$  edge of Fe and Ni.

A comparison of the experimental XANES spectra after 4 hrs in vacuum and 14 hrs in vacuum shows that the Ni spectrum does not change at all, whereas the Fe spectrum varies considerably. An inspection of the simulated spectra shows that the agreement with the experimental Ni spectrum can be obtained if the molecule **2** is released first and after 4 hrs in vacuum this process is completed within the probing depth of TEY detection, i.e. tens of nanometres. Release of the molecule **1** does not have further impact on the spectrum. This scenario is consistent with narrowing and shifting the center of gravity of the Fe  $L_3$  edge to lower energies between 4 hrs and 14 hrs in vacuum, when possible, the process of releasing of the molecule **1** occurs.

Thus, we can conclude, that the process of dehydration of  $(\text{H}_3\text{O})[\text{Ni}(\text{cyclam})][\text{Fe}(\text{CN})_6]\cdot 5\text{H}_2\text{O}$  in vacuum occurs with a certain order of releasing particular inequivalent water molecules, which could be determined from a comparison of changes in the experimental simulated Fe and Ni L-edges XANES spectra.

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