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Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** *Single crystal XRD structural analysis of extremely small crystals of molecular multiferroics and porous molecular magnets*	**Experiment number**: *SC-4651*
Beamline: *BM01*	**Date of experiment**: from: *03.10.2017* to: *04.10.2017*	**Date of report**: *22.12.2017*
Shifts: *3*	**Local contact(s)**: *Dr Vadim Diadkin*	*Received at ESRF:*

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Report:

From 03.10.2017 (8am) to 04.10.2017 (7am) a series of single-crystal diffraction experiments were performed for very small single crystal samples of high nuclearity molecular compounds (coordination clusters) and porous coordination polymers (including potential molecular multiferroics) at the Swiss-Norwegian Beamline BM01. Over 20 samples crystallizing in form of tiny single crystals (<50 μm) and/or having a very large unit cell (more than 50 000 $Å^3$) were selected. During the 3 shifts, the data for 18 single crystals were collected affording 15 crystal structures. The most important results are described below.

The first group of compounds that were investigated using the BM01 beamline were three-dimensional (3-D) cyanide-bridged bimetallic coordination networks incorporating additional bridging ligands connecting 3*d* metal ions – potential molecular multiferroics. The most interesting ones are $(NH_4)[(H_2O)Co^{II}\text{-}(\mu\text{-}HCOO)\text{-}Co^{II}(H_2O)][Nb(CN)_8]\cdot 3H_2O$ (**1**), $(NH_4)[(H_2O)Fe^{II}\text{-}(\mu\text{-}N_3)\text{-}Fe^{II}(H_2O)][Mo(CN)_8]\cdot 3H_2O$ (**2**), $[(H_2O)Mn^{II}\text{-}(\mu\text{-}HCOO)\text{-}Fe^{III}(H_2O)][Nb(CN)_8]\cdot 4H_2O$ (**3**) and $[(H_2O)Fe^{II}\text{-}(\mu\text{-}HCOO)\text{-}Fe^{III}(H_2O)][Nb(CN)_8]\cdot 4H_2O$ (**4**). Insertion of the additional ligand into the 3-D CN-bridged framework of these compounds is expected to induce magnetic frustration/spin-cantin, which will be studied using a SQUID magentometer. Studies of these type of compounds will lead to the discovery and understanding of the design prinicples of molecualar spin-ice materials. Especially $(NH_4)[(H_2O)Co^{II}\text{-}(\mu\text{-}HCOO)\text{-}Co^{II}(H_2O)][Nb(CN)_8]\cdot 3H_2O$ (**1**), which crystallize in the form of extremely small single crystals (<20 μm) is expected to show intriguing magnetic behavior due to the inherent magnetic anisotropy of Co^{II} ions. Additionally, as $(NH_4)[(H_2O)Co^{II}\text{-}(\mu\text{-}HCOO)\text{-}Co^{II}(H_2O)][Nb(CN)_8]\cdot 3H_2O$ (**1**) crystallizes in a polar *I*4cm space group with all hydrogen atoms of the formate anions oriented along the

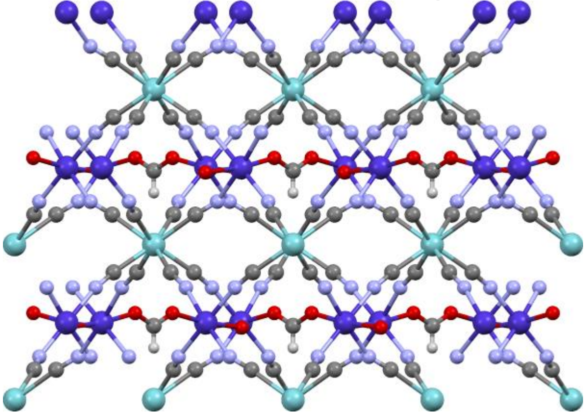

*Figure 2. Fragment of the polymeric structure of $(NH_4)[(H_2O)Co^{II}\text{-}(\mu\text{-}HCOO)\text{-}Co^{II}(H_2O)][Nb(CN)_8]\cdot 3H_2O$ (**1**) presented along the a direction.*

crystallographic *c* direction (Figure 1), it is considered a potential multiferroic – a compound combining magnetic and electric ordering. Its dielectric behavior will be studied soon.

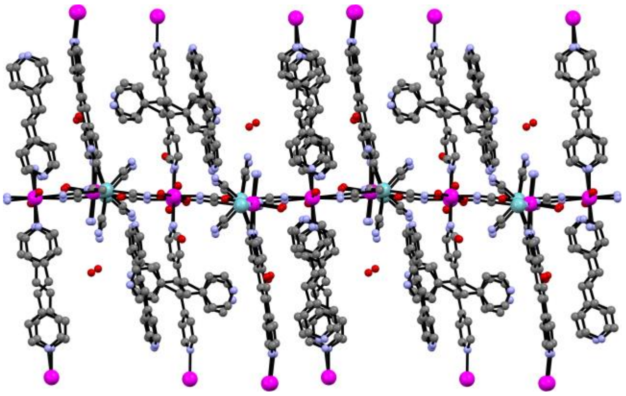

*Figure 2. Fragment of the crystal strcuture of $[Mn(H_2O)_2(dpe)]_8[Nb(CN)_8]_4\cdot18H_2O\cdot10dpe$ (**5**) presented along the b direction.*

We have also managed to determine crystal structures of several porous/magnetic sponge-like compounds, among them $[Mn(H_2O)_2(dpe)]_8[Nb(CN)_8]_4\cdot18H_2O\cdot10dpe$ (**5**) (dpe = trans-1,2-di(4-pyridyl)ethylene). It forms a structure of two-dimensional cyanide-bridged layers, pillared by the organic dpe ligands. Additional intercalated dpe molecules are located 3.7 Å from the bridging ones (Figure 2), providing an opportunity for observation of their 2+2 photocycloaddition upon UV light irradiation (respective experiments were already conducted and the photocycloaddition was confirmed by means of IR spectroscopy). Unfortunately, (**5**) crystallizes in a triclinic crystal system (*P*-1 space group) and the completeness of the crystal data is below 90% (only *phi* scans were possible due to the unavailability of the four circle goniometer).

The diffraction data for two-dimensional (2-D) cyanide-bridged Cu-$[W(CN)_8]$ layered multiferroics incorporating two different organic cations: triethylenediammonium ($dabcoH_2$) and imidazolium (imH_2) were also collected: $(dabcoH_2)\{Cu^{II}_2[W^{V}(CN)_8]_2\}$ (**6**) and $(imH_2)\{Cu^{II}[W^{V}(CN)_8]\cdot xH_2O$ (**7**). However, the thin plate-like crystals of both compounds suffered from heavy twinning and there are still on-going efforts to refine their crystal structures. Figure 3 presents the tentative structural models a layered of both compounds.

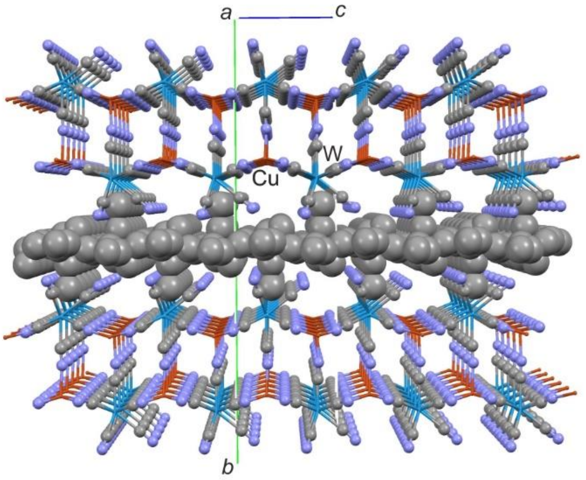

*Figure 3 The expected topology of (**6**) and (**7**).*

The most prominent results of our experiment are the crystal structures of a family of trimetallic nineteen-nuclear cage molecules exhibiting huge unit cells and large empty spaces filled with solvent molecules. The crystal structures have been solved and refined successfully: $Cu_6Ni_6Fe_7$ (**8**) and $Cu_6Mn_6Fe_7$ (**9**). These molecules belong to the family of molecular Prussian Blue analogues. Along with the not-yet-published $Co_{12}Fe_7$ cluster, which was studied by means of standard diffraction system equipped with a sealed-tube source, they are elegant examples of this intesively studied group of compounds. The presence of two different coordination sites within each cluster (octahedral and square pyramidal) enabled synthesis of mixed metal trimetallic clusters with Cu^{II} cations occupying square pyramidal positions and the high resolution synchrotron data enabled successful determination of their crystal structures.

The determination of the crystal structures of the originally proposed porous coordination polymers based on $[(NC)_7Mo^{IV}\text{-}CN\text{-}Pt^{IV}(L)_4\text{-}NC\text{-}Mo^{IV}(CN)_7]^{4-}$ (MoPtMo) was unsuccessful, due to the very poor quality of the crystals. The only samples suitable for X-ray diffraction appeared to be $(dppipH_2)_2[Mo(CN)_8]\cdot xH_2O$ (**10**) – a decomposition product.

The first papers describing the results obtained at BM01 will be published in 2018.