## PhD thesis at Institut Néel, Grenoble, France:

# The structure of coordination polymers studied by electron crystallography (3D ED)

**Summary of the thesis project**:

The aim of this thesis project is to solve the structures of coordination polymers using electron crystallography, and thus make a significant contribution to the search for new materials in this field. Indeed, for coordination polymers, as for any new material, determining the crystallographic structure is a key step in understanding their properties. In the case of coordination polymers, this determination is often a decisive limitation, as it is very difficult to obtain single crystals of sufficient size for X-ray diffraction. In this thesis project, we will use electron diffraction, since for this technique nanometric crystals are sufficient for solving the structures. A combination of methods and strategies from structural biology and materials science will enable us to optimize data acquisition and processing.

**Objectives:**

Solve coordination polymer structures by electron crystallography, enabling chemists to develop new materials. Combine electron crystallography methods from structural biology and materials science to optimize structure-solving procedures.

**Background:**

Coordination polymers are materials whose structure is made up of organic molecules and metal atoms. Their structures and thus properties can be controlled by the choice of molecules and metal atoms used, but also by the method of synthesis. The possible variations of these materials are therefore virtually infinite, and it's not surprising that they can be found in a wide variety of applications: catalysis, fuel storage (hydrogen, methane), carbon dioxide capture, proton conductors for fuel cells, photovoltaics, sensors and electronic materials.

The development of these materials and a detailed understanding of their properties is highly dependent on the ability to accurately determine their crystallographic structures. However, for most coordination polymers, it is notoriously difficult to obtain crystals of sufficient size and quality for structural determination by X-ray diffraction. As a result, a large number of potentially interesting compounds remain unexploited due to the difficulty of studying their structures.

When only sub-micrometer-sized crystals can be obtained, electron diffraction can take over from X-ray diffraction. In fact, electron diffraction is perfectly suited to the study of single crystals a few tens of nanometers in diameter, i.e. whose volume is more than a million times smaller than that required for single-crystal X-ray diffraction.

In recent years, impressive advances in the technical performance of transmission electron microscopes, and above all in the field of detectors, have led to significant advances in electron crystallography. Thanks to these fabulous advances, electron diffraction-based methods are now perfectly complementary to X-ray diffraction and neutron diffraction.

On the other hand, coordination polymers often have low resistance to irradiation. Here too, the use of electron diffraction is more favorable than that of X-ray diffraction, because it is only necessary to apply a quantity of irradiation $10^3$ to $10^4$ times lower than in X-ray diffraction to obtain the same useful signal [1].

Nitronyl nitroxide radicals functionalized with imidazole substituents and associated with transition metals are a good example of the difficulties mentioned above. With a great deal of effort on the part of our collaborator D. Luneau (LMI, Lyon), it was possible to obtain single crystals for X-ray diffraction of a few compounds, but for most of the synthesized compounds this was not possible. Interactions between the 5/2 spins of $Mn^{2+}$ ions and the ½ spins of nitronyl nitroxide radicals provide them with spin tautomerism behavior, i.e. their magnetic state can be driven by a change in temperature or irradiation. Despite these properties, which make them interesting for data storage, research into these coordination polymers was halted because the structures could not be determined.

We have therefore developed innovative tomographic electron diffraction methods that require only a very low irradiation dose (less than 1 $e^-/Å^2$) [2, 3]. The experimental data generated by these methods are of very high quality, enabling not only the resolution of structures, but also their refinement by taking into account the dynamic effects of electron diffraction.

Small size and sensitivity to irradiation are also characteristics of crystals in structural biology. Although the difficulties are comparable, they have led to different experimental and data processing solutions in the two fields. In collaboration with researchers at the Institut de Biologie Structurale, we are exploring synergies in the combination of different methods in order to optimize the data acquisition strategy and its exploitation. For example, exploratory work has shown that it is possible to solve the structure of a coordination polymer by applying a method commonly used in structural biology: molecular replacement (article submitted).

In this thesis, the student will be trained in the use of the transmission electron microscope and the application of low-dose 3D ED methods to various coordination polymers. The student will collaborate with chemists who synthesize the coordination polymers and biologists who provide know-how on the methods used in their field. The aim is to optimize the experimental parameters of the technique and to solve the structures of the relevant MOFs synthesized by our collaborators in Lyon.

[1] "*The potential and limitations of neutrons, electrons and X-rays for atomic resolution microscopy of unstained biological molecules*", R. Henderson, Quarterly Reviews of Biophysics 28, 2 (1995), 171-193 (link)

[2] **"***Low-dose electron diffraction tomography (LD-EDT)", S. Kodjikian and H. Klein,* ***2019****, Ultramicroscopy, 200, 12-19* (link)

[3] "*Dose Symmetric Electron Diffraction Tomography (DS-EDT): Implementation of a Dose-Symmetric Tomography Scheme in 3D Electron Diffraction*", E. Yörük, H. Klein, S. Kodjikian, 2024, *Ultramicroscopy*, **255**, 113857, https://doi.org/10.1016/j.ultramic.2023.113857

**PhD thesis:**

For his/her research work, the PhD student will be integrated into the Institut Néel's MRS team. He/she will carry out 3D electron diffraction experiments on the state-of-the-art transmission electron microscope (TEM) (commissioned in 2022), equipped with a direct-detection camera and a fast C-MOS camera, as well as a module for precession-mode electron diffraction. The Institut Néel's transmission electron microscopy platform also includes a dedicated sample preparation area. The software required for data processing is also available in the laboratory. The synthesis of MOF materials will be carried out by our collaborators in Lyon.

The thesis will comprise several stages:

- Performing electron diffraction experiments in a transmission electron microscope under low-dose conditions on coordination polymers.
- Optimization of experimental conditions to obtain diffracted intensity sets of the highest quality.
- Combining data processing methods from structural biology and materials science.
- Structural resolution of coordination polymers from 3D ED data.
- Structure refinement from 3D ED and/or X-ray powder diffraction data.

This thesis will be part of two ongoing collaborations:

The collaboration with Dominique Luneau (LMI, Université Claude Bernard Lyon 1) concerns the synthesis of new coordination polymers with two- or three-dimensional structures for which structure determination by X-ray diffraction is not possible (ANR MagDesign in progress), as well as measurements of the compounds' magnetic properties.

Collaboration with Dominique Housset and Wai Li Ling (IBS, Grenoble) involves the pooling of crystallographic methods from the fields of structural biology and materials science. The synergy created by combining methods from both communities enables us to solve previously inaccessible structures.

**Expected results:**

This doctoral work will lead to the resolution and refinement of several coordination polymer structures, enabling significant advances in the synthesis of new materials. The combination of methods from structural biology and materials science will enable us to optimize both the data acquisition method to obtain the best quality data using the lowest dose, as well as the data exploitation.

**Profile and required skills**:

- Master in Physics, Solid state chemistry or instrumental physics.
- Basic knowledge in crystallography and diffraction
- Knowledge in transmission electron microscopy would be appreciated

Application deadline: 23rd of May 2024

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