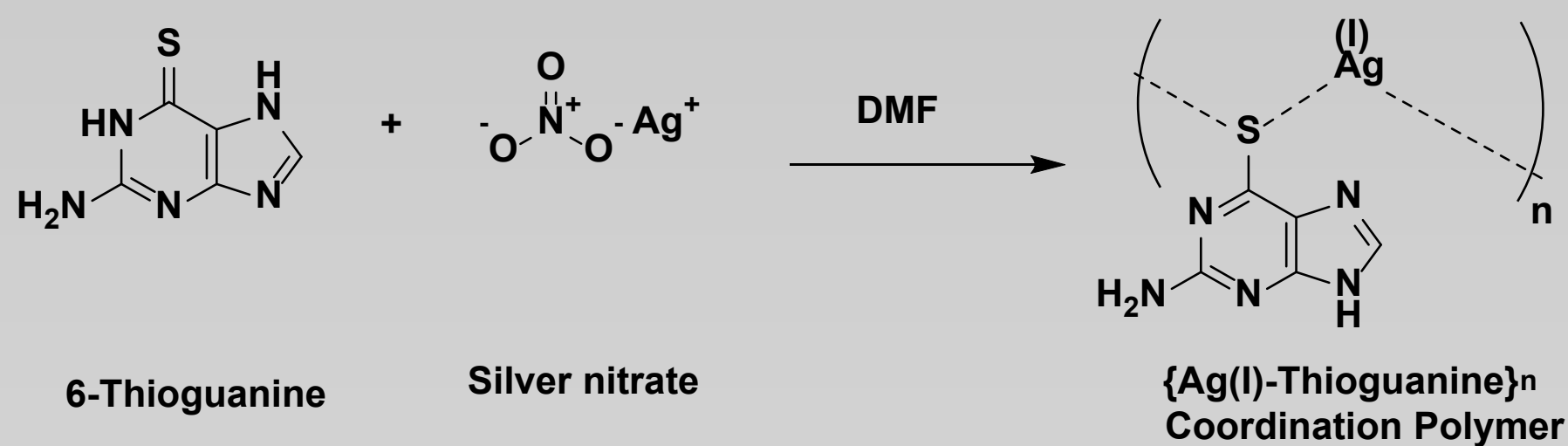


Synthesis and Characterisation of DNA Component Nanomaterials from Silver/Gold/Copper nanoparticles.

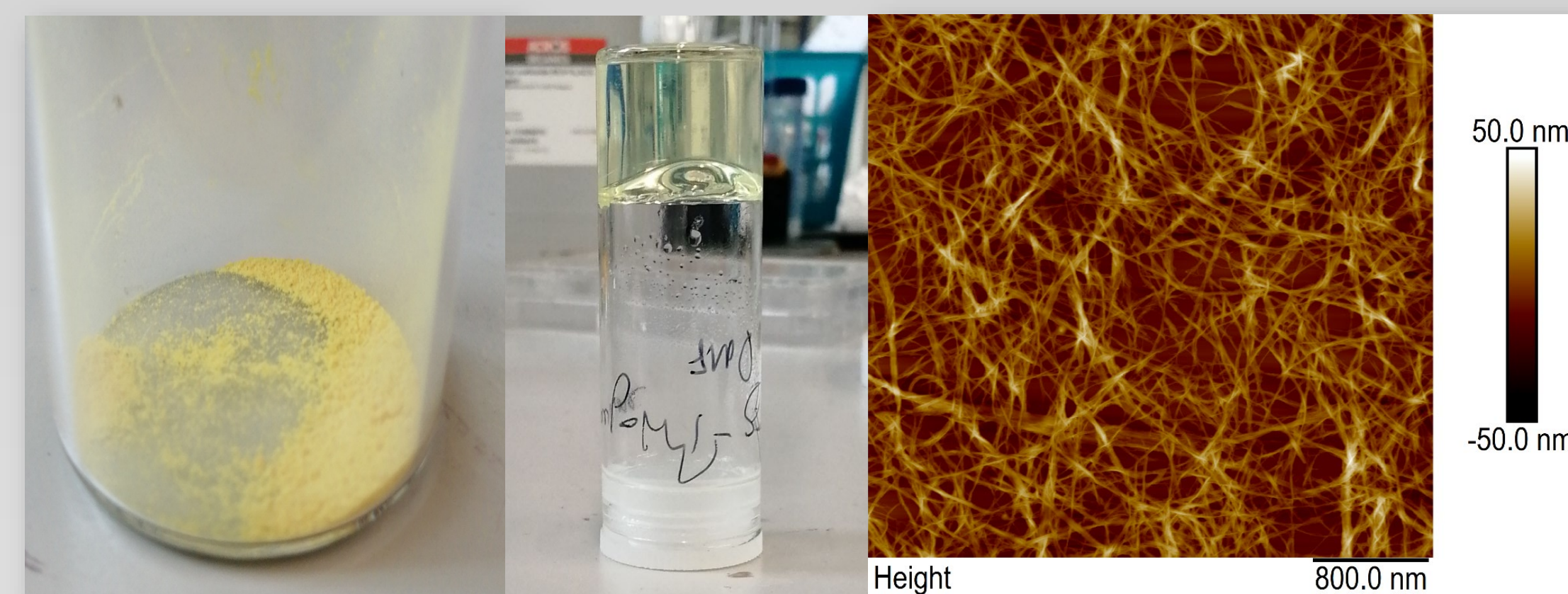
The Aim of this project was to investigate methods to synthesise and characterise nanomaterials using $\text{Ag}^+/\text{Au}^+/\text{Cu}^+$ salts with Thio-Nucleobases, Thio-Nucleosides, Nucleobase, Nucleosides and Nucleotides.

The most effective way of characterising these Metallo DNA coordination complexes is by X-Ray crystallography, therefore, the aim was not only to synthesis these complexes but to form crystalline forms of the compound.

6-Thioguanine Complexes

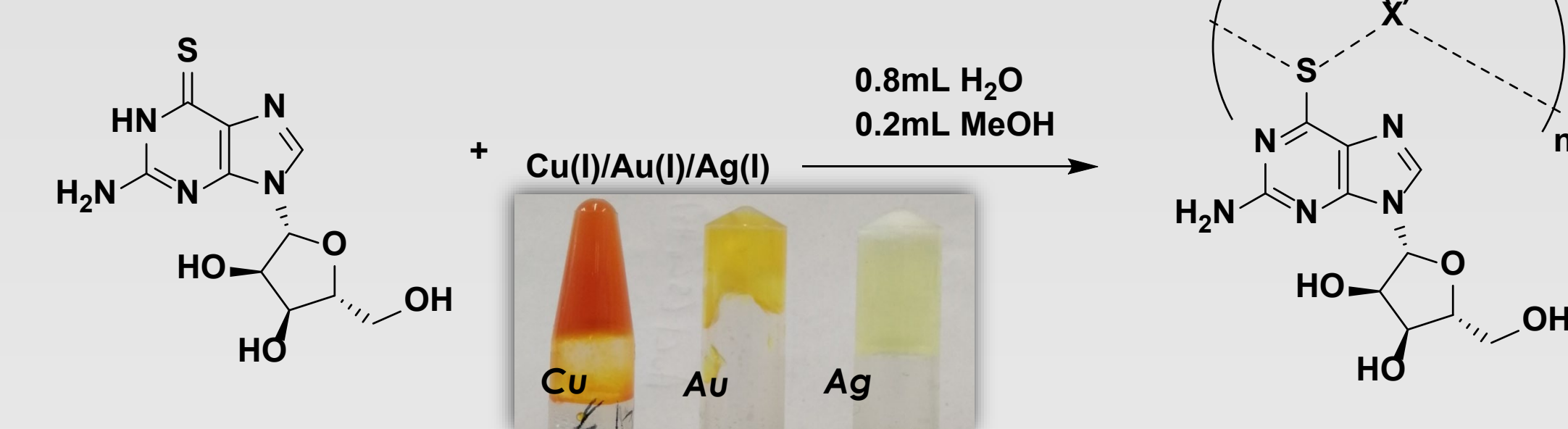


At room temperature, 6-thioguanine dissolved in Dimethylformamide with the aid of sonication, reacts readily with Ag^+ ions from the silver nitrate to form coordination polymer. The product can be observed as a powder or a Gel.



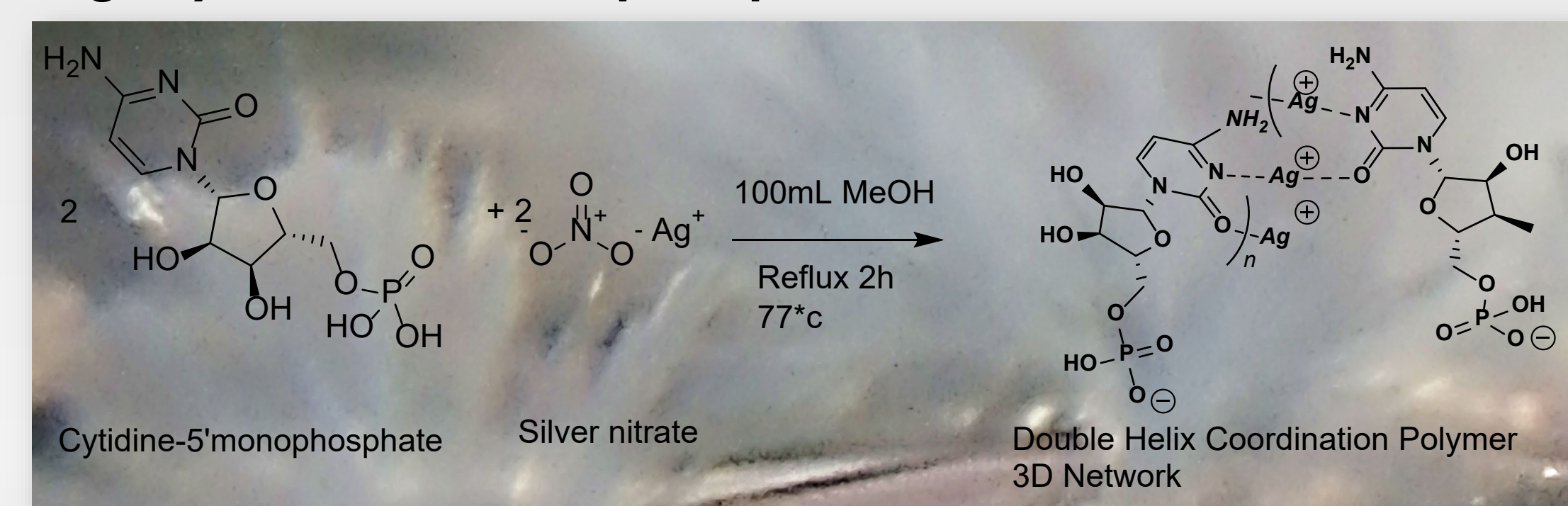
(Right) the powder form of Ag-6-thioguanine, (Middle) the Gel form of the complex and (left) is an Atomic Force Microscope image of the Gel. As the AFM shows, the 1D nanowires interlock and form a 3D network held together by the solvent.

6-Thioguanosine Gels



The reaction between 6-thioguanosine with the Copper, Silver and Gold nanoparticles via the salt reagents, would form 3D network of the coordination polymer. The ratio of solvent to complex is predominantly solvent. These Gels placed into between silicon filters and washed through with solvents, it was found that methanol could be used to wash the counter ions out of the structure.

Ag-Cytidine-5'-monophosphate

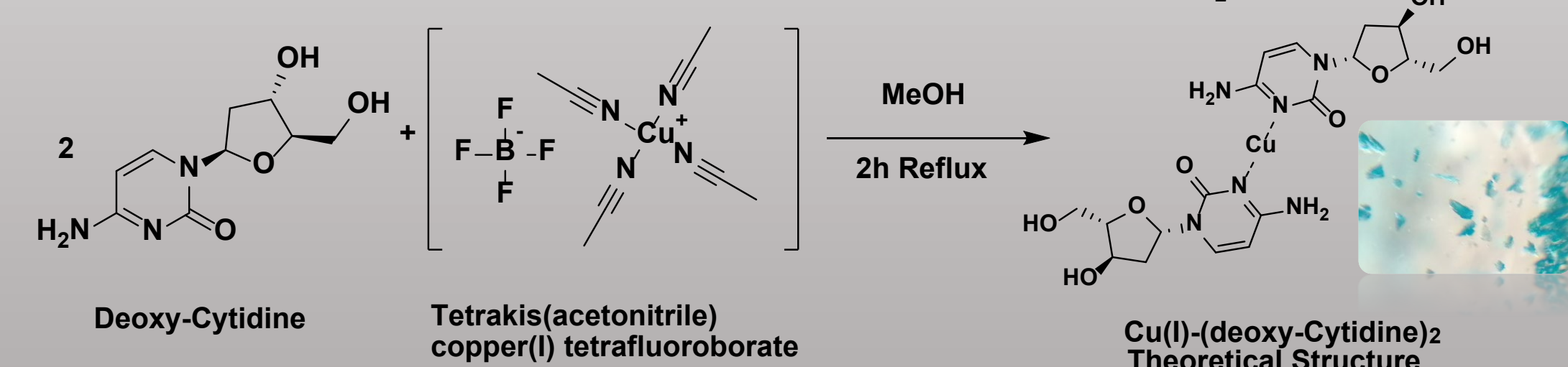


This experiment reproduced crystal structure obtained by Liam Mistry, X-Ray crystallography confirmed by Unit Cell Check. Silver (I) ion binds across the N3 and O2 heteroatoms to form a coordination polymer. A Third interaction is observed with the O7' of the phosphodiester resulting in a 3D Coordination Network.

Cu(I) analogues of Ag(I) deoxy-Cytidine complexes

The Crystal structures of Ag Cytosine/ Cytidine and Deoxy Cytidine are known, discovered by PhD student Liam Mistry (Addressing the properties of "Metallo-DNA" with a Ag(I)-mediated supramolecular duplex† DOI: 10.1039/c8sc05103h). The Aim for this aspect of the project was to make analogues of these structure using Cu(I) instead of Ag(I).

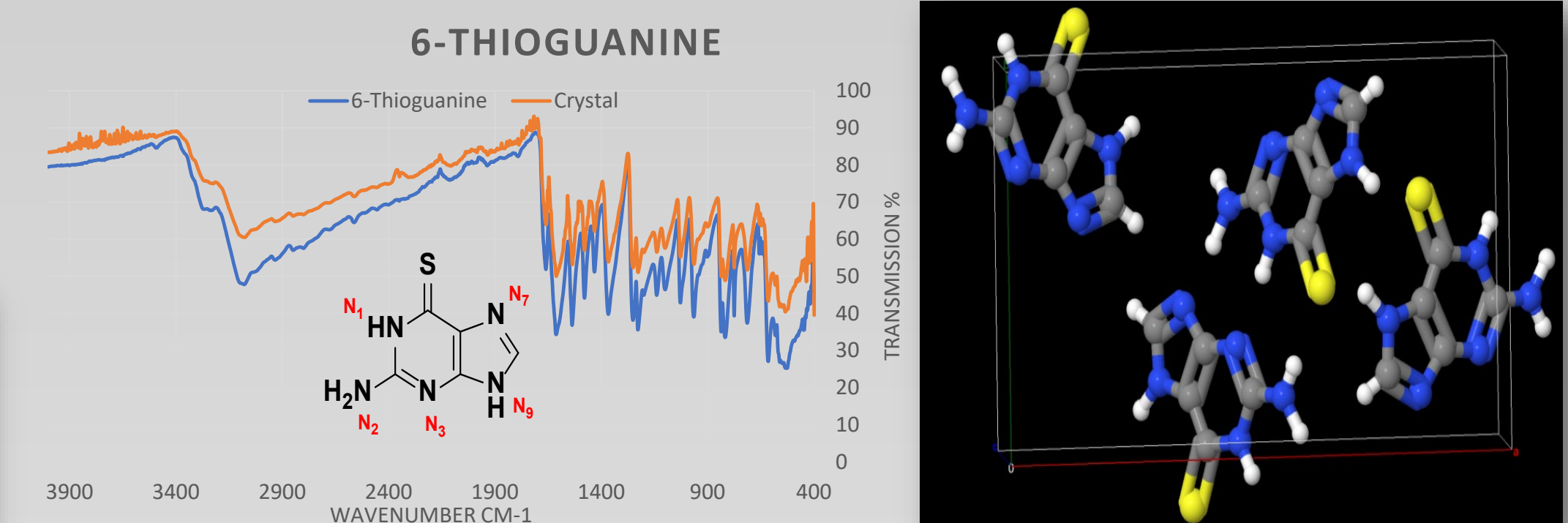
Problem with Cu(I) for these reactions, Cu(I) is unstable in aqueous conditions, more stable in methanol, although Cu(I) is very stable in acetonitrile however, the Cytosine or Deoxy Cytidine are not soluble in MeCN. Cu(I) can also be oxidised by the O_2 in the air.



This produced polyamorous crystals. Unconfirmed structure and requires further evidence.

Hydro/Solvo-thermal Reactions

This involved using an Autoclave and temperature gradient oven. The Autoclave contained a Teflon container which the reactants and solvent are placed within. The autoclave would enable conditions above the solvents natural boiling point due to pressure of expanding gases the remaining solvent remains in the liquid phase. This in turn increased polarity of the solvent and increased the solubility of the Ligand.

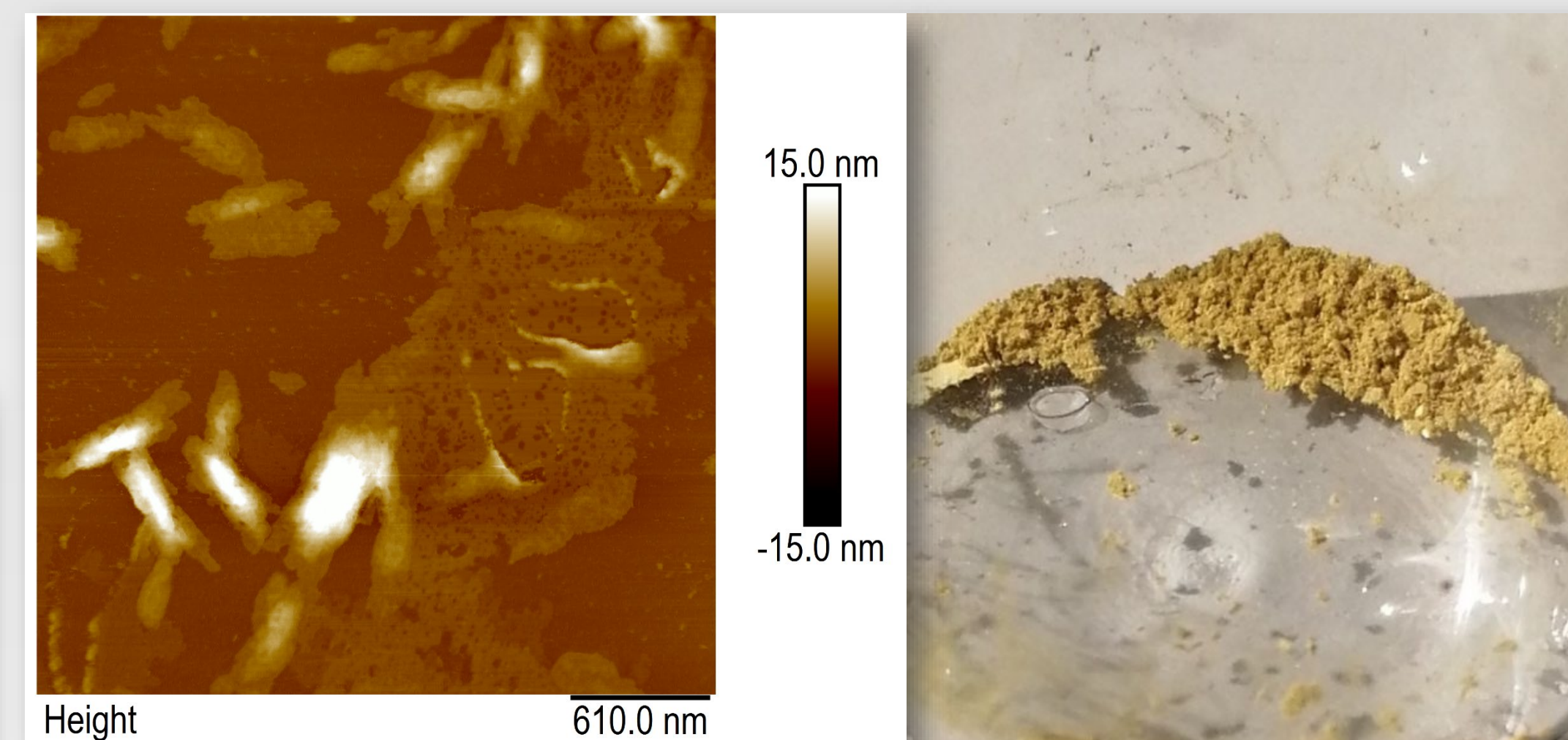
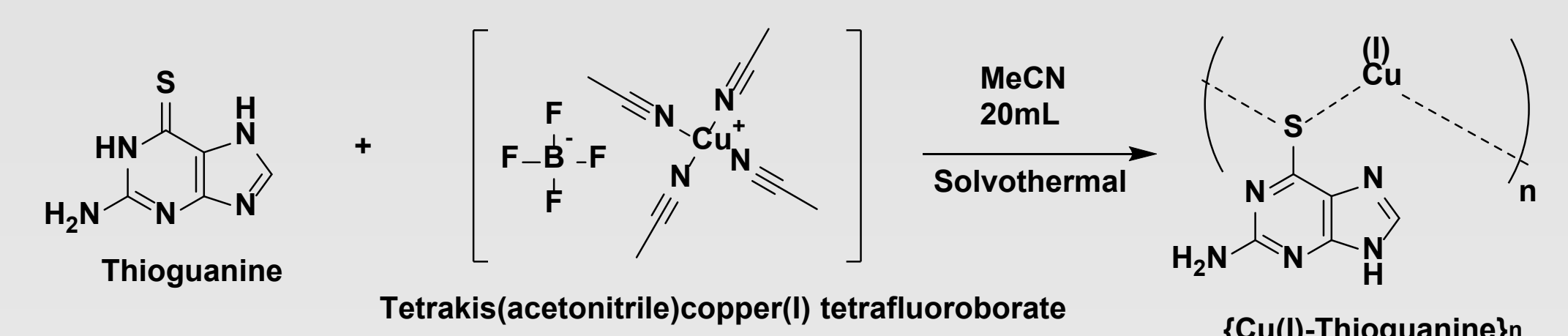


The Ligand of the coordination complex Thio-Nucleobase called 6-thioguanine, this was tested in the hydrothermal conditions at 160°C for 3 days and then cooled at a gradient of $0.1/\text{min}$. This produced crystals of the ligand, the unit cell shown above, image from The Cambridge Crystallographic Data Centre.

These conditions were then superimposed on to the reaction of the coordination polymer using $\text{AgNO}_3 / \text{CuOAc} / [\text{Cu}(\text{MeCN})_4][\text{BF}_4]$ salts with little success. The silver salt reduces under the conditions and the Copper(I) is oxidised to Copper(II).

However, the hydrothermal conditions when the solvent was switched to Acetonitrile which promotes Cu(I) stability, it was possible to isolate Cu(I)-thioguanine powder which hadn't isolated yet.

2-Dimensional Sheets of Cu-6-Thioguanine



2D sheets can be seen on the Atomic Force Microscopy Image (Left), the measure height of the single sheet is 1.8-2.4nm. The powder obtained from the reaction (Right).

Red diamond crystals analysis by X-ray crystallography although the diffraction observed from the lab source was insufficient to collect data, indications were that use of a synchrotron source may be worthwhile. The sample has been placed in the queue for the next beamtime allocation for DLS.

The Red colour of the crystal is promising sign of a Cu(I) complex similar to the gel observed in the 6-thioguanosine Copper (I) complex. As the AFM indicates above the complex has 2D sheet structure, whereas, the 6-thioguanosine Copper (I) complex has a core 1D polymeric chain with intermolecular interactions with solvent resulting in 3D network.

Awaiting the DLS results, to determine the coordination chemistry of the Cu(I) in this complex.

Acknowledgements

Thank you to the Nanoscience Lab for their support and supervision in my further development of my research skills during this placement, Professor Andrew Houlton, PhD student Liam Mistry and PhD student Pablo Rojas Martinez.