Poster

Use of 3D-ED as a Tool for Studying Mechanism of Formation of Complex Materials

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3D-electron diffraction (3D-ED) is one of the fastest growing areas of crystallography [1] due to its ability to yield structure solutions from crystals two to three orders of magnitude smaller than is generally possible with X-rays. In previous work we have shown that it is a very useful tool for investigating polymorph evolution during crystal growth of glycine [2] and carbamazepine [3], enabling sampling of solid forms after crystallisation times as short as 20 seconds. This work focuses on the use of electron diffraction for the insight it can provide on the mechanism of formation of polynuclear transition metal complexes.

In contrast to studying small organic molecules, I am investigating the reaction between FeF_3 and pyridine which are refluxed in methanol for three hours. This forms the complex $(PyH)_5\cdot[Fe_{13}O_4F_{24}(OMe)_{12}]\cdot 4H_2O\cdot CH_3OH$, also known as Fe_{13} which is shown in Fig. 1 [4]. The complex structurally resembles a fragment of the mineral magnetite encased by ligands. In one experiment, a reaction was set up and allowed to proceed for 1 hour. Then an aliquot was taken from the reaction mixture, micro-filtered onto a TEM grid, and allowed to evaporate.

A number of different crystallites were observed on the grid using the new electron crystallography facilities of the National Crystallography Service at the University of Warwick, and though the analysis of these is on-going, one extremely exciting and significant result is already apparent. A well-formed crystallite was identified to be magnetite itself (*Fd-3m*, $a = 8.39$ Å, $R_1 = 13\%$). This has important implications for the mechanism of the reaction, suggesting hydrolysis of the halide constitutes the initial step. This is initiated by a low concentration of water in the solvent, and presumably yields nuclei of magnetite which then become solvated by MeOH.

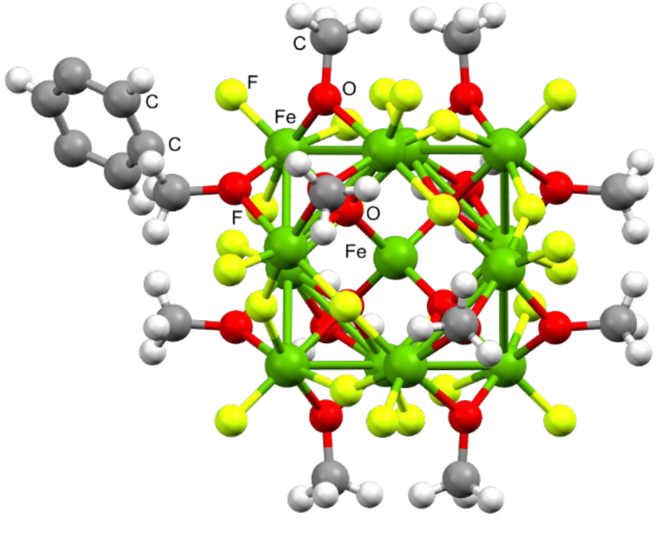

Figure 1. Structure of the Fe_{13} anion.

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