

A Sheet of Clusters: Self-Assembly of a (4,4) Network of Fe^{III}₁₀ Clusters

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Supplementary Information – Mössbauer Spectroscopy

The Mössbauer spectrum of **1** at 78 K (Figure 3a) appears as a broad symmetrical doublet with an isomer shift, δ , of ~ 0.47 mm s⁻¹ with respect to α -Fe at room temperature, and a quadrupole splitting, Δ , of ~ 0.78 mm/s. However, the fit is clearly inadequate, with significant failures in the wings, the centres of the peaks and the centre of symmetry. Knowing that there are multiple iron sites, fits to multiple overlapping subspectra which are not resolved, need to be carefully justified. Accordingly, fits were attempted with from two to seven doublets, with the initial parameters being put in with the same isomer shift and approximately equally spaced quadrupole splittings. There is, of course, no reason why the quadrupole splittings should be equally spaced, but it was assumed that the fitting routine should deal with that.

The goodness-of-fit parameter, χ^2 , showed a continual decrease through all the increases in the number of doublets. However, if one used MISFIT then the value of the MISFIT parameter, M , decreased almost linearly on a log scale up to five doublets, after which it deviated sharply downwards for six doublets and then to a position significantly above the linear extrapolation for seven doublets. The error in MISFIT, ΔM , varied smoothly on a log scale for all the fittings. However, for one to four doublets, we always had $M > \Delta M$, so that the range of M did not include zero, which is the criterion for a valid fit. For five doublets, we had $M = \Delta M$ ($= 0.00099$), making it the first valid fit. For six and seven doublets, we had $M < \Delta M$, with the discrepancy for six doublets being over an order of magnitude. Such a result indicates that it is a very good fit, but that the theory is not being tested very stringently. This behaviour leads us to the conclusion that the fit to

five doublets is justifiable as the best fit, independent of any knowledge of the crystallography.

All the doublets had the same isomer shift of 0.47(1) mm/s which is typical of high-spin Fe(III). The quadrupole splitting, linewidth (FWHM) and area of the doublets were, starting from the outermost doublet: 1.33(4) mm/s, 0.39 mm/s, 17(5)%, 1.03(3) mm/s, 0.30 mm/s, 20(9)%; 0.79(3) mm/s, 0.28 mm/s, 22(9)%, 0.56(4) mm/s, 0.30 mm/s, 22(9)% and 0.32(5) mm/s, 0.37 mm/s, 19(7)%. The errors in these parameters are all large because they are not mathematically orthogonal. However, it is notable that all the areas are very close to being equal to 20% without any adjustments. This equal area situation was not the case for any of the other fits, being 1:2 for two doublets, 1.0:1.5:1.5 for three doublets, 1.0:1.5:1.4:1.4 for four doublets and 1.2:1.0:1.4:1.7:1.5:1.5 for six doublets providing further confidence in the validity of the fit. At this stage, it is not possible to associate any of the doublets with a particular crystallographic site.

X-Ray Powder Diffraction

Bulk purity of **1** was confirmed by comparison of calculated vs. experimental X-ray powder diffraction spectra (Figure S1). The calculated spectra was generated using the program Mercury from the low temperature single crystal data.¹ Experimental data was collected using a Phillips diffractometer at room temperature, equipped with carbon-monochromated Cu radiation. Minor differences in peak positions are observed due to the temperature difference of the samples. Very large, spurious peaks in the experimental data are an artifact of the sample plate as shown in Figure S2.

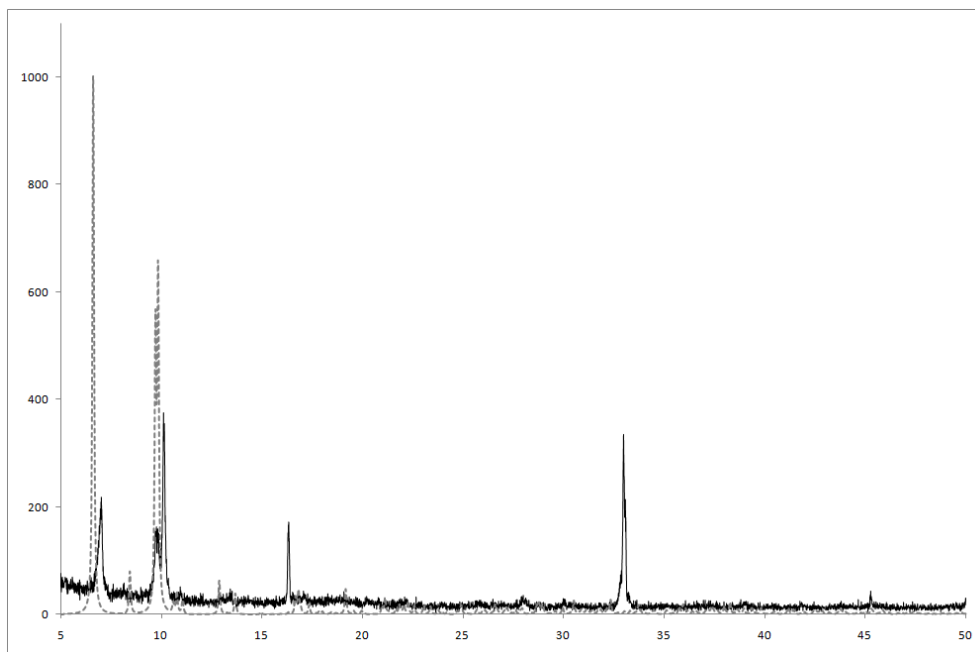


Figure S1: Comparison of experimental room temperature powder X-ray diffraction spectra (solid black line) with the calculated pattern from the low temperature single crystal experiment (grey dashed line).

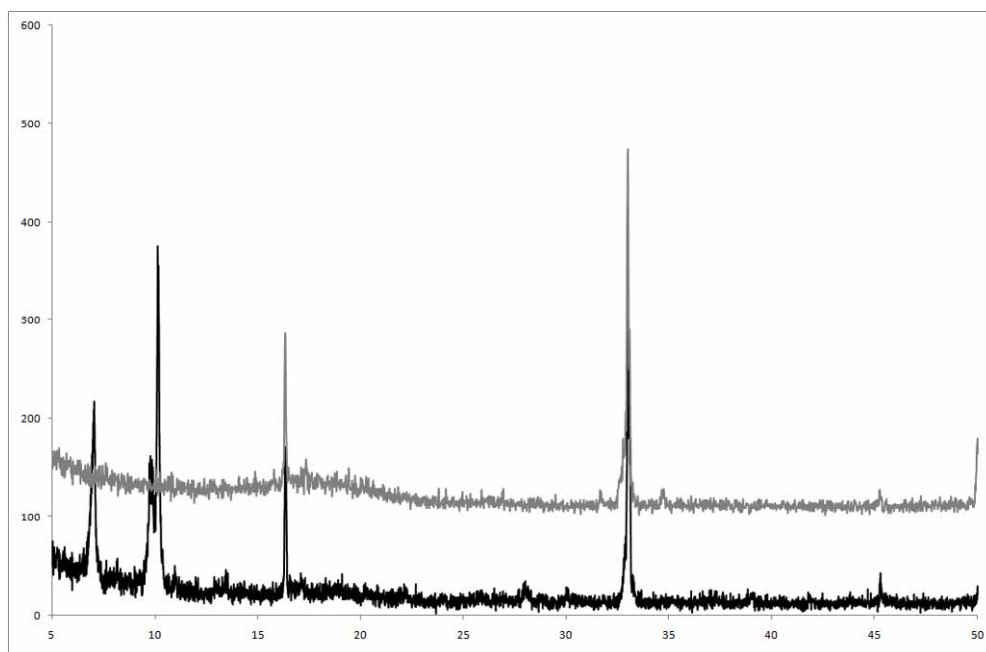


Figure S2: Peaks due to the sample plate are present in the experimental spectra of **1**. Black = **1**, Grey = amorphous sample showing only peaks due to the plate.