

# “Unpublishable” Data: Does My R-factor Look Big in This?

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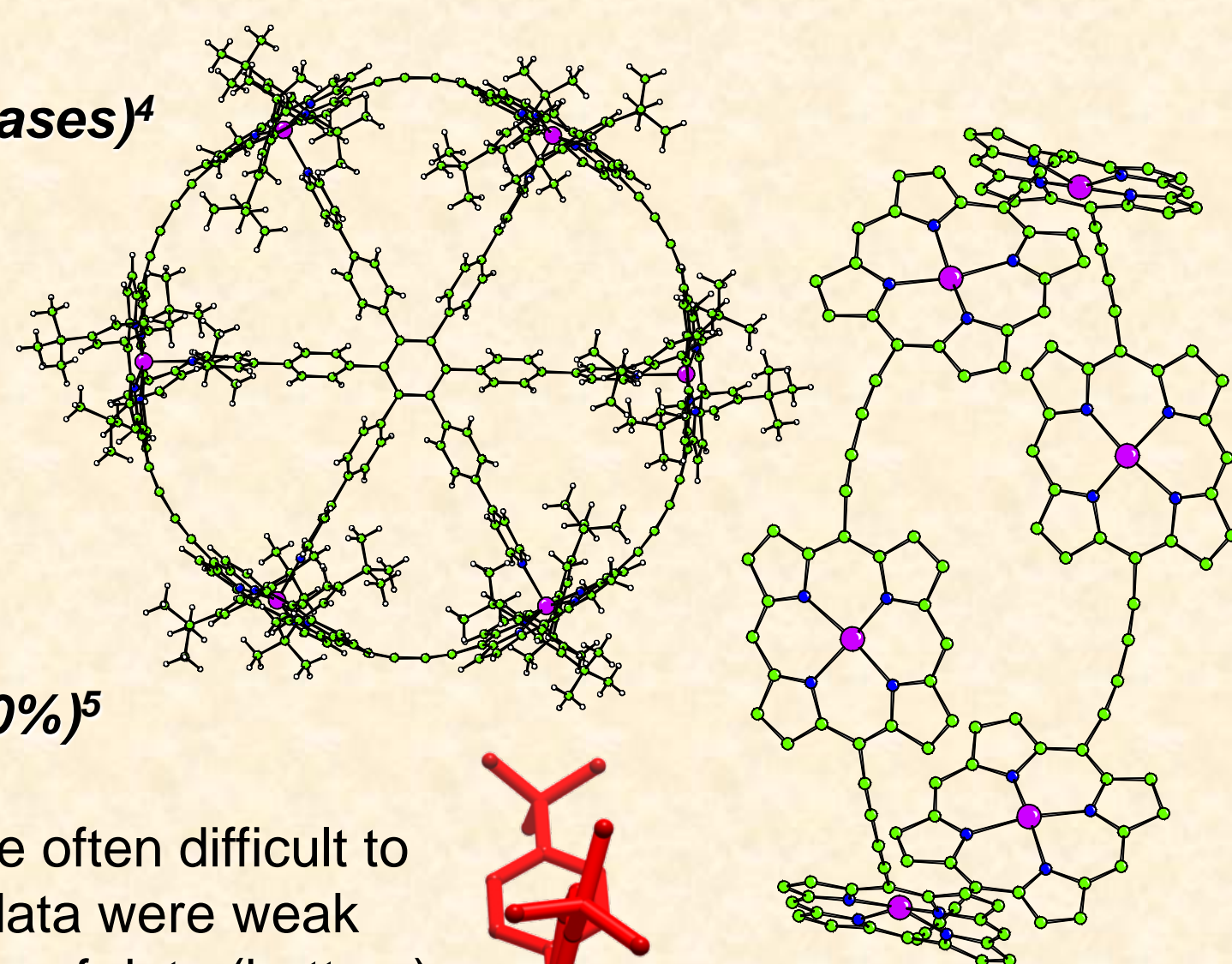
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## Weak and Incomplete Data

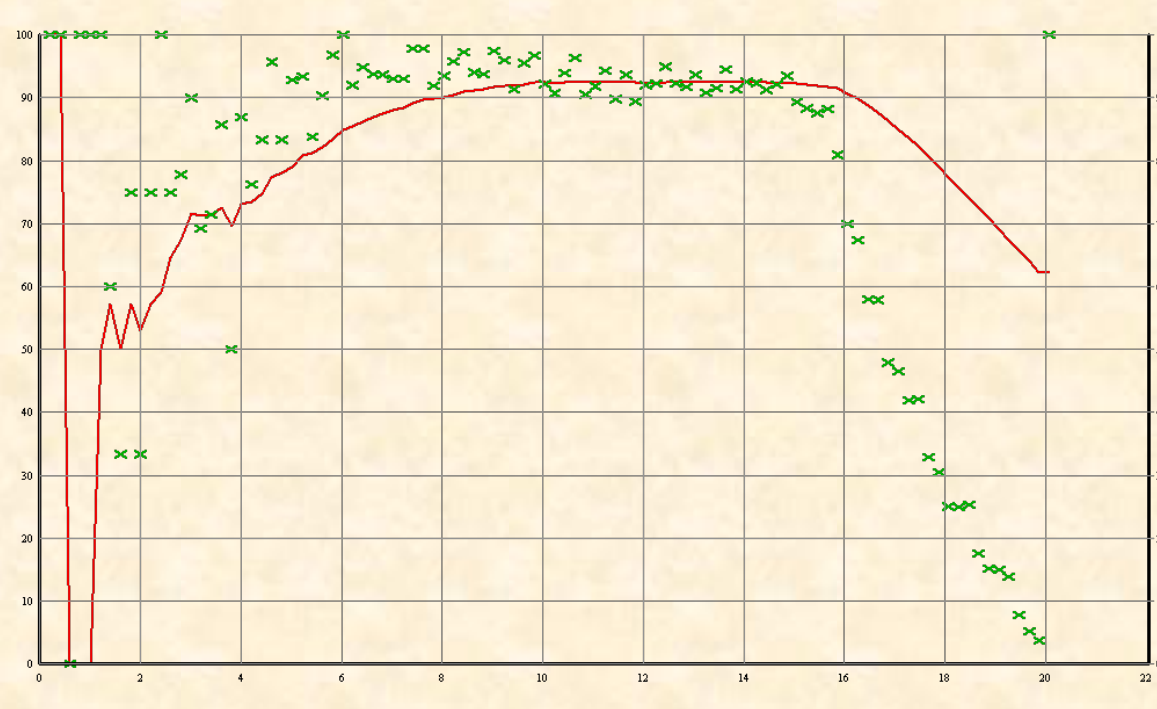
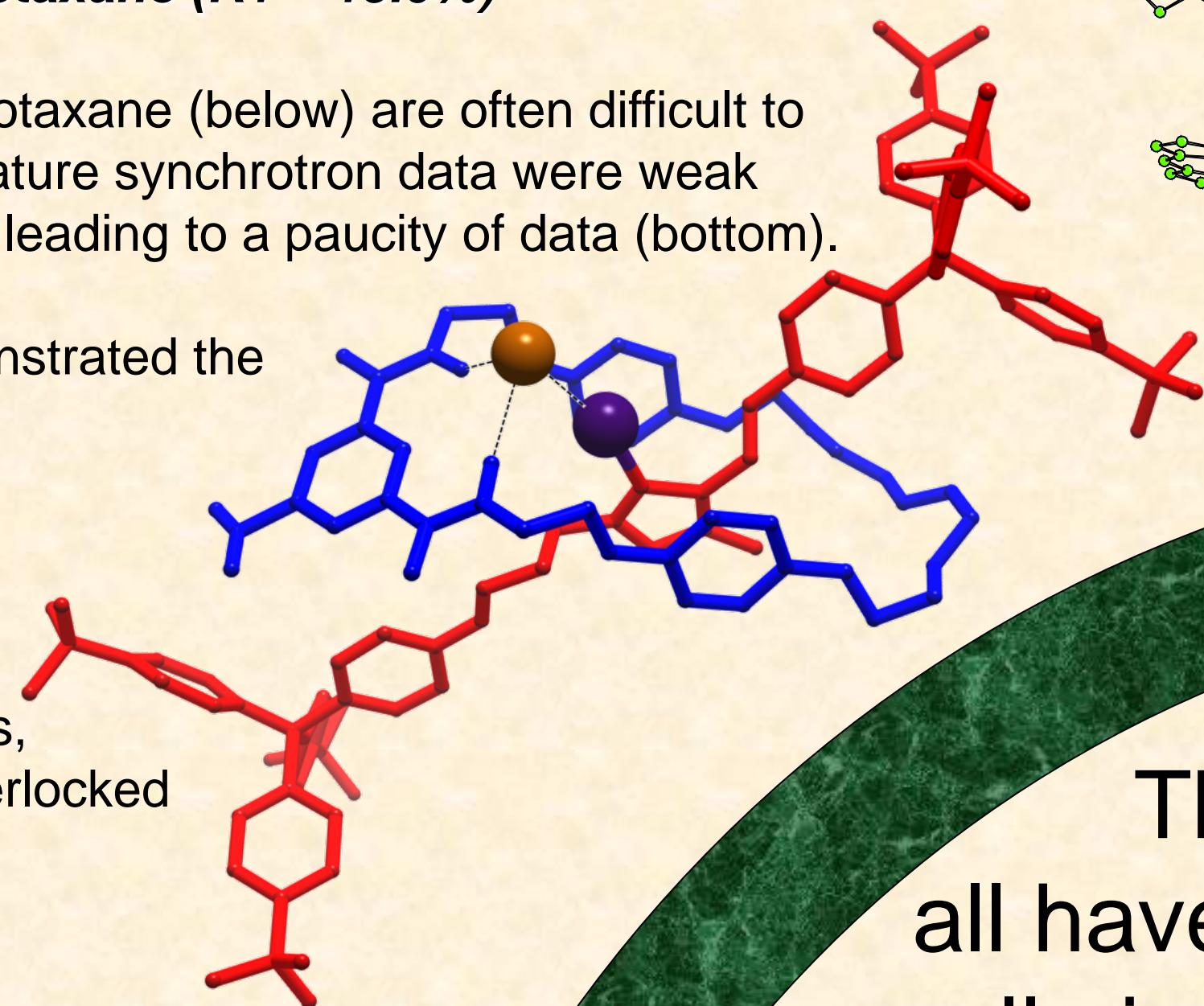
### Case Study 1: Porphyrin Wheel ( $R1 = 13.1\%$ ; $I > 2\sigma(I)$ in all cases)<sup>4</sup>

- This structure had more than half a dozen attempts (on I19 at Diamond Light Source), but never scattered beyond c. 3 Å.
- The suspected third polymorph yielded sufficient data to solve and refine the structure (right) although it was disordered, lacking in data and contained diffuse solvent.



### Case Study 2: Halogen-bond Templated Rotaxane ( $R1 = 15.0\%$ )<sup>5</sup>

- Crystals of interlocked structures like this rotaxane (below) are often difficult to grow and diffract poorly. Even low temperature synchrotron data were weak and the sample suffered radiation damage leading to a paucity of data (bottom).
- The structure solved, but refinement demonstrated the whole macrocycle (blue), and many of the terminal tBu groups were disordered together with diffuse solvent in the void.
- Final refinement had a data to parameter ratio of 3.63 : 1 and required 4401 restraints, but clearly showed the presence of the interlocked structure and the weak Br...I bond which was the purpose of the study.



Shell completeness is shown in green; the cumulative completeness in red

The structures shown here all have some “problems” and almost all give Level A checkCIF/PLATON<sup>2</sup> alerts, but these do not ultimately affect the conclusions drawn. The key feature is that although the data are not “squeaky clean”, they are

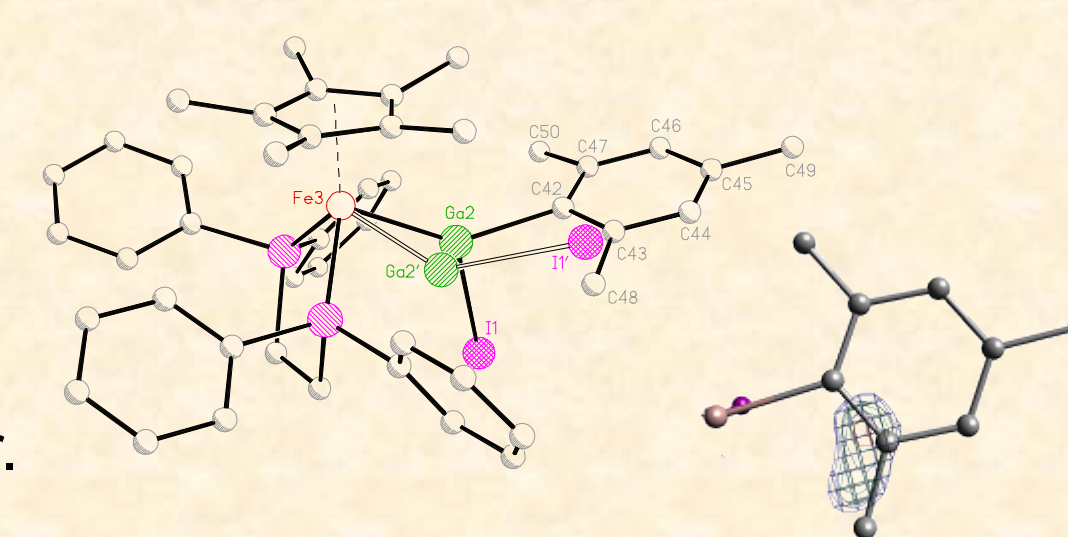
## Fit For Purpose.

Where possible, crystal structures should always be published with the chemistry, as that is their raison d'être, and in context, bad structures have supporting evidence. The real problem is not the quality of the crystallographic data, but the attitude that a crystal structure is always correct; famously, Zhong and Liu<sup>3</sup> proved this is not the case. As scientists, we must avoid “crystallographic arrogance” and examine all available data.

## Large Residuals and Even Larger Voids

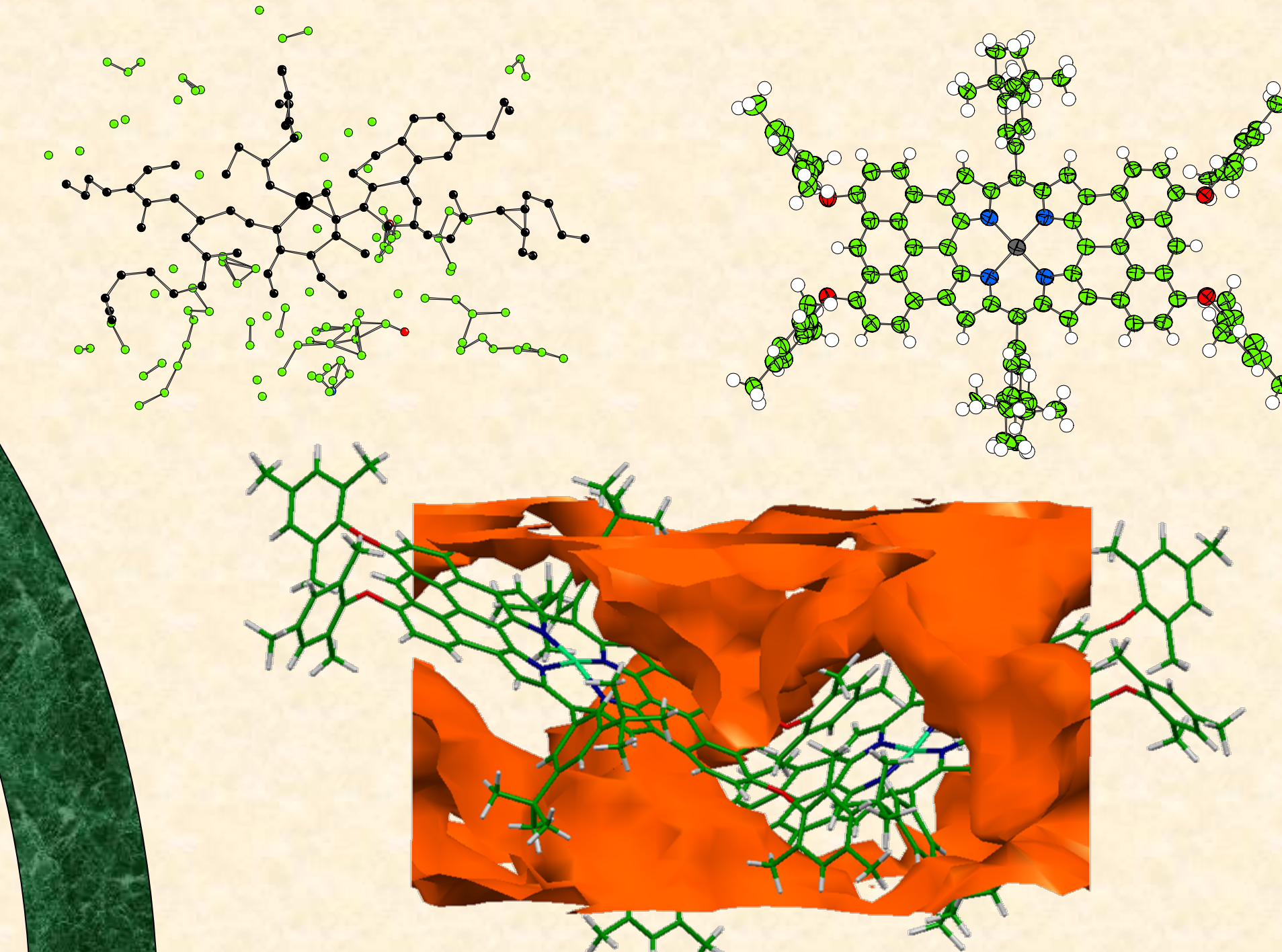
### Case Study 3: Terminal Gallylene Complex ( $R1 = 8.3\%$ ; $\rho_{max} = 4.5 \text{ e.}\text{\AA}^{-3}$ )<sup>6</sup>

- The structure exhibits two large peak of residual electron density which disrupt refinement of the mesityl group. The distance between them and Fe3 are very similar to those for Fe3-Ga2 and Ga2-I1 suggesting disorder.
- Efforts made to model the disorder including fixing the isotropic ADPs and refining the occupancy (constraining the total gallium/iodine to unity) gave an occupancy of 3.6% for the minor component. Refinement was unstable and made only a small difference to the agreement factors.



### Case Study 4: Anthracene-fused Porphyrin ( $R1 = 14.0\%$ )<sup>6</sup>

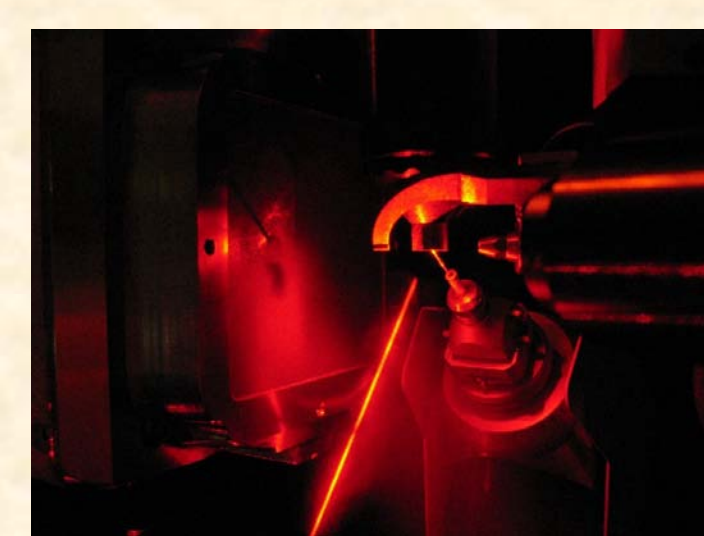
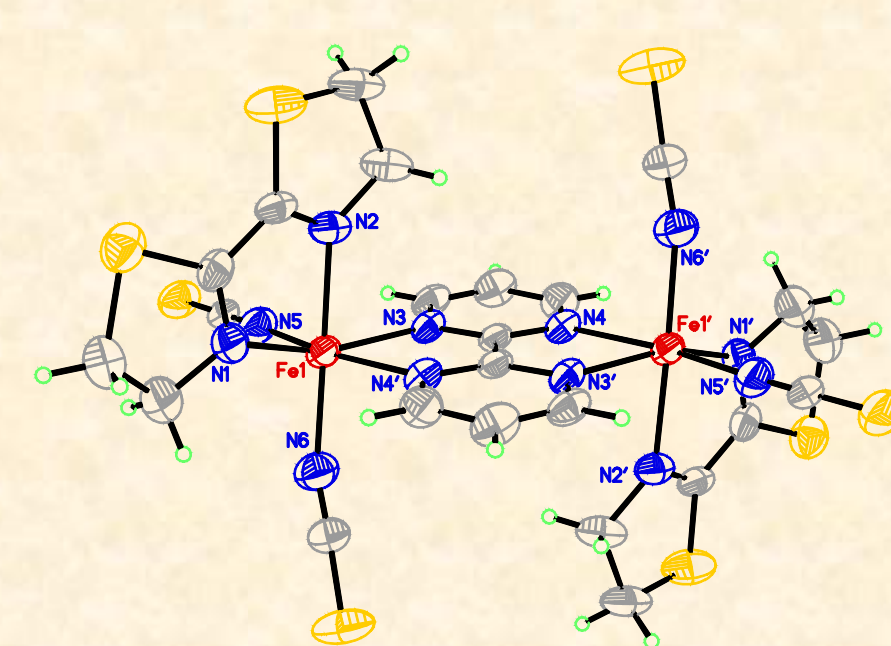
- Synthesis involved making the anthracene substituted porphyrin and coupling the rings together to form the extended aromatic structure. Crystals were so thin that they broke on contact and lost solvent very fast.
- Data were collected on I19 at Diamond, but were still very weak. The structure solved (below left), but required many restraints to control it. Although the conditions were far from ideal (>50% void; some low angle reflections missing), the only way to treat the diffuse solvent was to use PLATON/SQUEEZE.<sup>2,7</sup> The ring system is unquestionably planar, confirming that the coupling was successful.



## Marginal Results

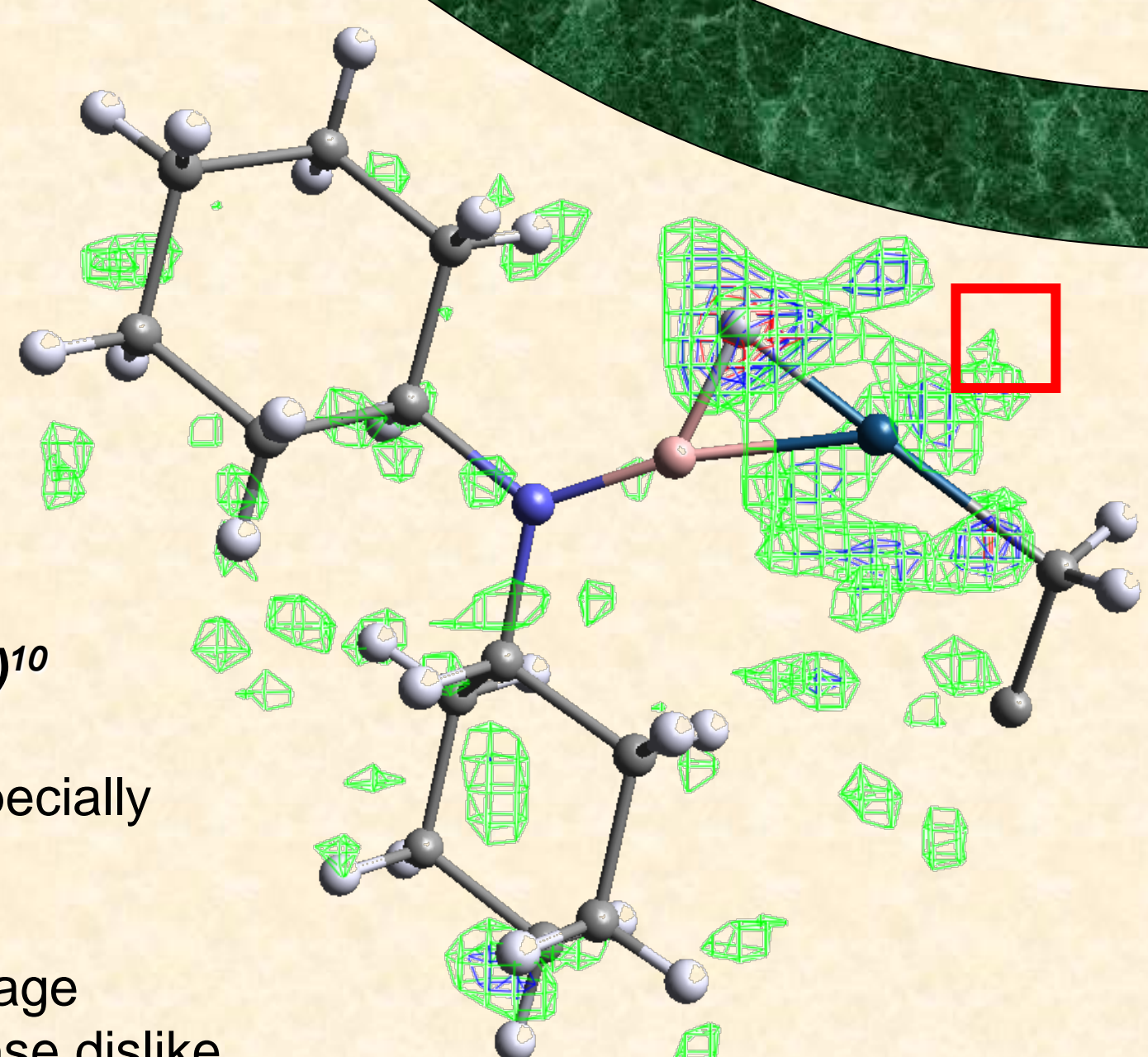
### Case Study 5: Iridium Hydride Complex<sup>8</sup>

- Classically, locating hydrogen atoms can only be done with neutron data, but truncating the data can tidy up the difference map giving insight into hydrogen atom positions.<sup>9</sup>
- Careful examination of the difference Fourier map for the iridium complex (below right) showed a peak, not in the obvious vacant site (shown as a red box), but alongside the borylene ligand.
- This was later supported by strong evidence for a direct B—H interaction from <sup>11</sup>B and <sup>1</sup>H NMR and infrared spectroscopy measurements.



### Case Study 6: Dinuclear Spin Crossover Complex ( $R1 = 17.3\%$ )<sup>10</sup>

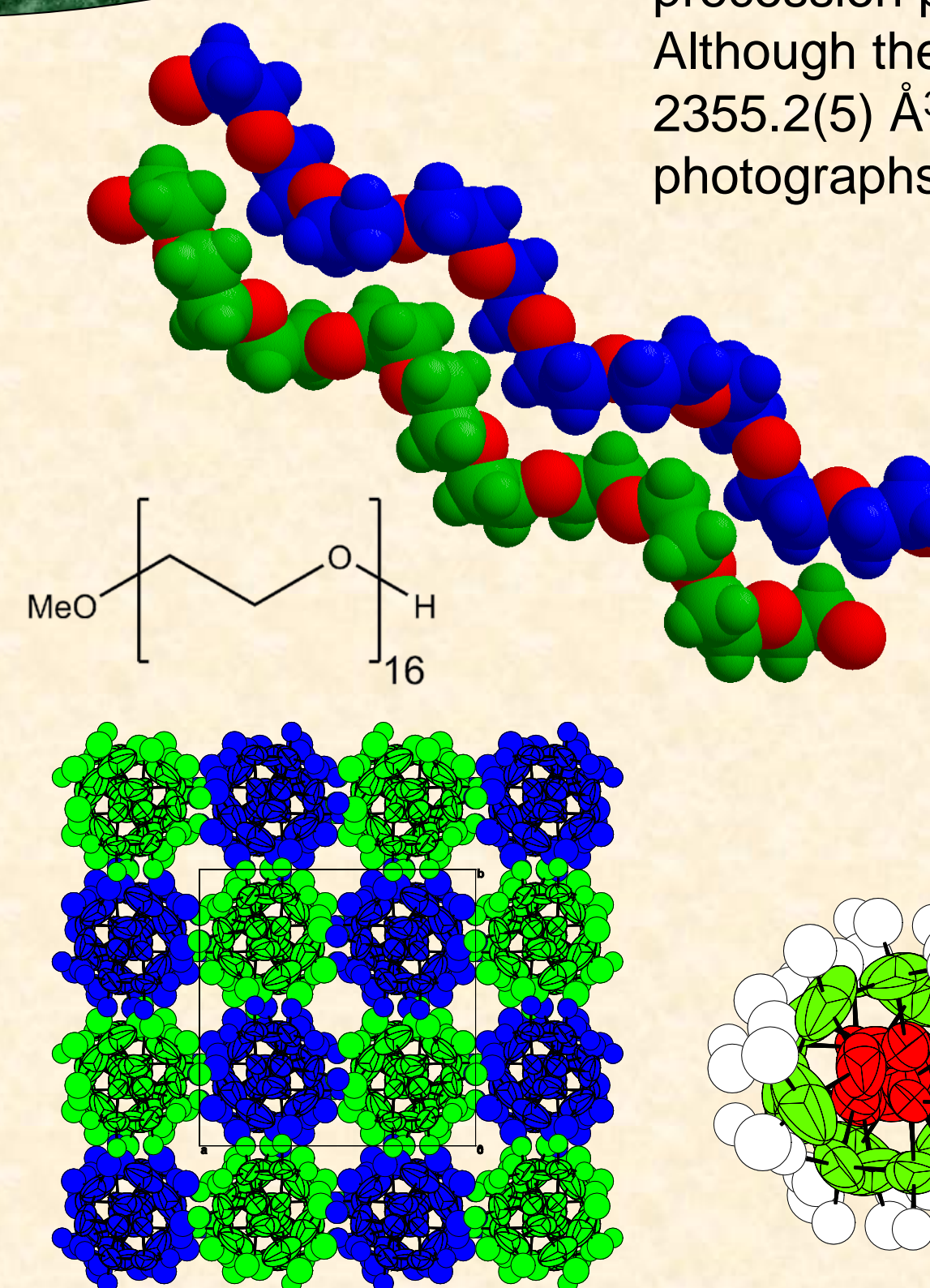
- In situ diffraction measurements are notoriously challenging, especially very low temperature excited state trapping experiments.
- The dinuclear spin-crossover complex (above left) suffered damage on cooling through the high-low spin transition and showed intense dislike for both 633 nm and 532 nm and it was necessary to irradiate it at 830 nm, during the data collection.
- The metastable high spin structure did not solve ab initio, but refined from the low temperature data.
- The errors on the diagnostic Fe-N bond distances and associated octahedral volume were large, but despite the large R-indices, it was possible to be confident that the structure was that of the high spin state from the unit cell parameters alone.



## Mystery Symmetry

### Case study 7: Polyethylene Glycol ( $R1 = 14.0\%$ )<sup>11</sup>

- Crystals of this solvated sixteen unit polyethylene glycol diffracted poorly and were only solid at room temperature because it was highly monodisperse. In situ recrystallisation experiments were unsuccessful. Data collected conventionally on laboratory instrumentation were processed with a monoclinic cell of 12.805(2) Å, 12.821(2) Å, 15.697(2) Å,  $\beta = 113.958(7)^\circ$ ,  $V = 2355.1(6) \text{ \AA}^3$ .
- Remarkably, it solved by in  $P2_1$  using SIR92,<sup>12</sup> yielding a continuous structure consisting of 59 atoms and a dominant O—C—C—O motif (below). Additional symmetry was evident, and ADDSYM<sup>2,13</sup> suggested space group  $C222_1$  [12.805(2) Å, 28.689(4) Å, 12.821(2) Å,  $V = 4710.0(2) \text{ \AA}^3$ ].
- Examination of the structure suggested that it was really tetragonal and study of simulated precession photographs suggested that the cell was smaller in the a and b directions. Although the chosen I-centred tetragonal cell (9.0621(11) Å, 9.0621(11) Å, 28.680(5) Å,  $V = 2355.2(5) \text{ \AA}^3$ ) appeared to index the data, it was clear from simulated precession photographs that there was additional intensity between the reflections.



- This could indicate a larger cell, diffuse scattering (caused by disorder), or modulations due to the period of the molecule which is incommensurate with the period of the cell. The structure was reprocessed as I-centred tetragonal and solved *ab initio* in I-4 with the final structure in I-4c2.
- The model published does not give a complete description of the structure and even with the low symmetry  $P2_1$  model, there is no indication of the ends of the PEG. The primary features of model, namely the helical nature of the molecule, the anti-parallel packing (shown in blue and green, left) and the oxygen atoms in the centre of the helix are in no doubt.

1. Betteridge, P.W., Carruthers, J.R., Cooper, R.I., Prout, K. & Watkin, D.J. (2003). *J. Appl. Cryst.*, **36**, 1487.  
2. PLATON, A Multipurpose Crystallographic Tool, A. L. Spek, Utrecht, the Netherlands, 1998; A. Spek (2003). *J. Appl. Cryst.* **36**, 7-13.  
3. Harrison, W. T. A., Simpson J., and Weil, M. (2010). *Acta Cryst.*, **E66**, e1-e2.  
4. Hoffmann, M., Kärbbratt, J., Chang, M.-H., Herz, L.M., Albinsson, B. & Anderson H. L. (2008). *Angew. Chem. Int. Ed.*, **47**, 4993-4996; Kondratiuk D., Sprafke, J. *et al.*, *manuscript in preparation*.  
5. Kilah, N. L., Wise, M. D., Serpell, C. J., Thompson, A. L., White, N., Christensen, K. E. & Beer, P. B. (2010). *J. Amer. Chem. Soc.*, *in press*.  
6. Coombs, N. D., Aldridge, S *et al.* (2008). *J. Amer. Chem. Soc.*, **130**(47), 16111-16124.

7. van der Sluis P. & Spek, A. L. (1990). *Acta Cryst.*, **A46**, 194-201.  
8. Tang, C. Y., Thompson, A. L. & Aldridge, S. (2010). *J. Amer. Chem. Soc.*, *in press*.  
9. Cooper, R. I., Thompson, A. L. & Watkin, D. J. (2010). *J. Appl. Cryst.*, *in press*.  
10. Gaspar, A. B., Reiman, S., Güttlich, P., Thompson, A. L., Goeta, A. E., Muñoz M. C. & Real, J. A. (2006). *Chem. Eur. J.*, **12**(36), 2989-2998.  
11. French, A. C., Thompson, A. L. & Davis, B. J. (2008). *Angew. Chem. Int. Ed.*, **47**, 4993-4996.  
12. Altomare, A., Casciarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori G. & Camalli M. (1994). *J. Appl. Cryst.* **27**, 435.  
13. Le Page, Y. (1998). *J. Appl. Cryst.*, **21**, 983.