

Poster Presentations

[MS45-P03] Puzzling Negative Difference Density in Metal-Complex Crystal Structures.

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We present some case studies of structures with metal centers surrounded by bulky ligands with unexplained negative difference density at the metal site. One plausible reason could be the partial incorporation into the crystal of the ligands without the metal ion. This could arise when the packing is dominated by bulky ligands, often used to stabilize unusual bonding situations, thus leading to nonstoichiometric defects similar to those commonly found in minerals that are responsible for the spectacular colors of many gemstones. Now that it is becoming standard practice to display the difference density during refinement using guis such as *shelXle* [1], rather than working with just a list of peaks, it is difficult to overlook such warning signs (of course protein crystallographers always look at such density maps). However, this is not the only possible explanation of such unexpected difference density. Alternatives are **(a)** incorrect element assignment, **(b)** the use of incorrect *f* values as a result of an error in the wavelength, **(c)** radiation damage, and **(d)** the use of spherical neutral atom scattering factors rather than aspherical charged atom scattering factors. We are currently investigating which of the five possible explanations is correct. Albeit preliminary, the analysis highlights the importance of the submission of the (preferably unmerged) data to go with the crystallographic model.

In this respect, small-molecule crystallography has been lagging behind protein crystallography, impeding the scientifically desirable redetermination of all published small-molecule crystal structures when new methods become available (as has been done for macromolecular refinement by PDB_REDO [2]).

[1] Huebschle, C., Sheldrick, G. M., & Dittrich, B. (2011). *J. Appl. Crystallogr.* **44**, 1281-1284.

[2] Joosten, R.P., Salzemann J., Bloch, V., Stockinger, H., *et al.* (2009). *J. Appl. Crystallogr.* **42**, 376-384. **Keywords:** nonstoichiometric defects; aspherical charged atom scattering factors; data deposition