Ab initio structure solution of a new zeolitic imidazolate framework

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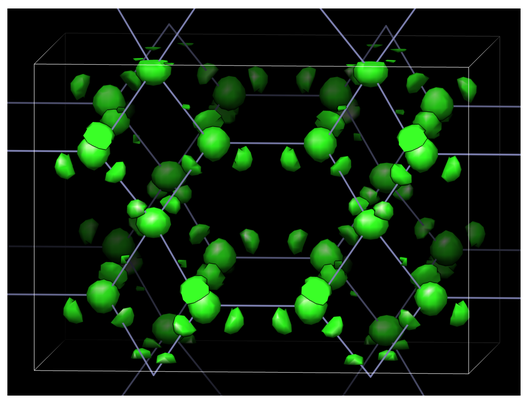
Introduction

Zeolitic imidazolate frameworks (ZIFs) are a class of metal-organic frameworks that are topologically analogous to zeolites. They are interesting because of their potential application in CO_2 capture and storage. Crystals are non-toxic, easy to manufacture and chemically and thermally stable [1]. A new ZIF has been synthesised with the chemical formula $Zn(MeIm)_2 \cdot (MeIm)_{1/2} \cdot (H_2O)_{3/2}$ (MeIm = methylimidazole). X-ray powder diffraction data were collected at a wavelength of 0.8250 Å with a Mythen-II detector on the Powder diffraction beamline at the Australian Synchrotron.

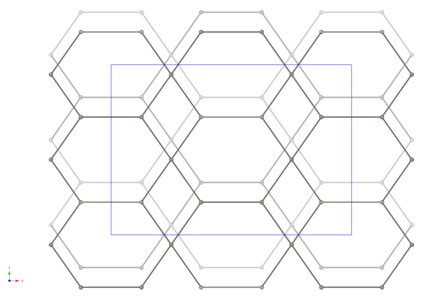
Powder diffraction data

- Eliminates noise
- Eases Pawley peak fitting (Topas [2])
- Intensities better suited for structure solution
- Refine against original data in final stages

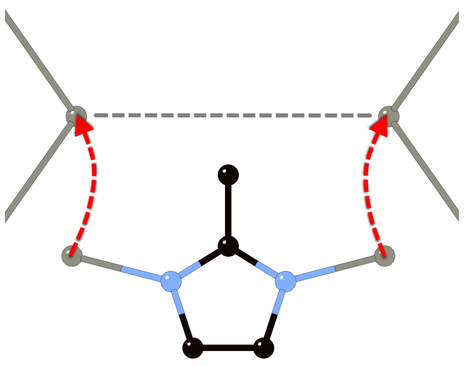
Approach to structure solution



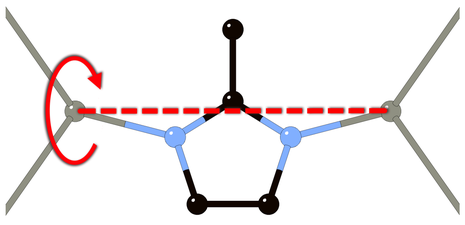
- Structure solved using Superflip [4]
- Only Zn locations could be located in density map
- Extract Zn framework atoms



- Zn atoms form 2D tetrahedrally 3-connected layers
- Zn—Zn distance of 6.0 Å typical for ZIF



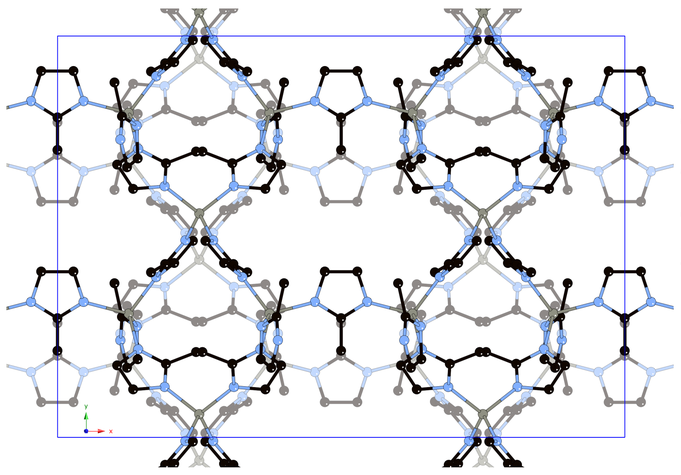
- Fit $Zn_2(MeIm)$ rigid body fragments to Zn atoms
- 4 independent MeIm fragments



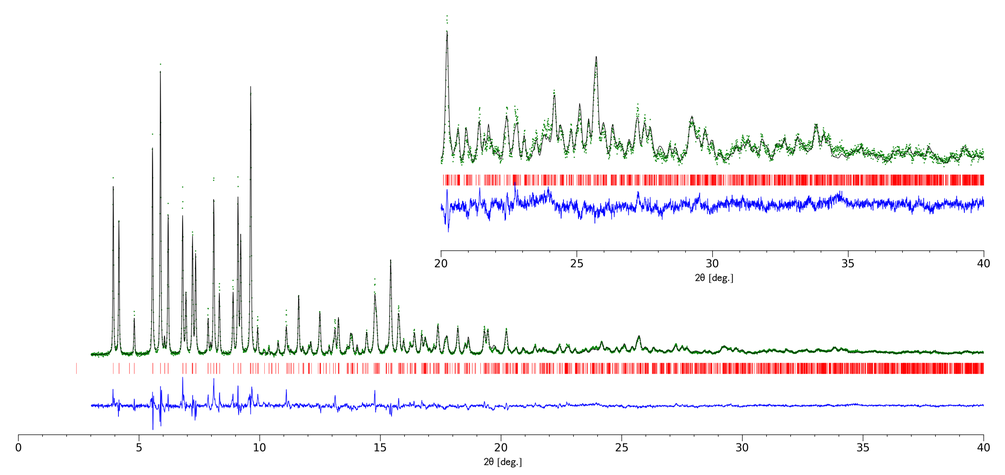
- Allow rotation of MeIm around Zn—Zn axis
- Fix Zn positions
- Reduce refinement to a 4 parameter problem
- Randomize starting rotations to avoid local minima

One of the MeIm molecules is only connected to one Zn atom, so the framework is "interrupted". The channel system is not very open, and this is consistent with the the measured adsorption capacity. The structure of this new phase also nicely explains its good performance in the separation of CO_2 and CH_4.

Final structure & refinement



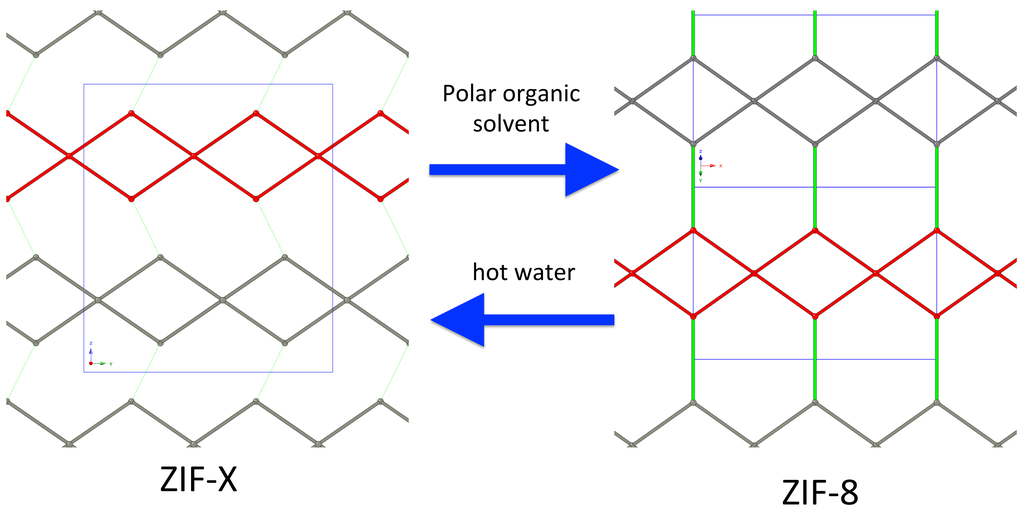
Orthorhombic unit cell
a = 24.0610 Å
b = 16.9673 Å
c = 19.6783 Å
Space group *Cmce*



- Non-framework atoms located in difference map (not shown)
- Refined using Topas [2] / XRS82 [5]
- R_F = 0.05; wR_p = 0.138; R_{exp} = 0.09

Comparison to ZIF-8

ZIF-8: cubic; *a* = 16.993220 Å; *I-43me*
ZIF-X and ZIF-8 can be converted into one another



References
[1] Park K.S., Ni Z., Côté A.P., Choi J.Y., Huang R., Uribe-Romo F.J., Chae H.K., O'Keeffe M., and Yaghi O.M., *Proc. Nat. Ac. Sc.,* 2007, 103(27), 10186.
[2] Coelho A., 2007, TOPAS-ACADEMIC v4.1, http://www.topas-academic.net/
[3] Savitzky A., Golay M.J.E., *Analytical Chem.,* 1964, 38(6), 1627.
[4] Palatinus L., Chapuis G., *J. Appl. Crystallogr.* 2007, 40, 786.
[5] Baerlocher, C. *The X-ray Rietveld System (XRS-82), a set of computer programs for the Rietveld refinement of X-ray powder data*, 1982.