Metal-Organic Frameworks, Hydrogen Bonded Organic-Frameworks

Jesse Rowsell
1977-2015
Outline

1. Who am I?

2. Who was Jesse Rowsell?

3. What is the crystalline structure of tcpb?

4. Who are our students?

NSF-MRI Grants
NSF-Grant # 1111896
Oberlin Chalk Walk
Publications as an undergraduate student

“Crystallographic investigation of the Co-B-O system”
J.L.C. Rowsell, N.J. Taylor and L.F. Nazar

“Structure and ion exchange properties of a new cobalt borate with a tunnel structure “templated” by Na+”
J.L.C. Rowsell, N.J. Taylor and L.F. Nazar

“Layered lithium iron nitride: a promising anode material for Li-ion batteries”
J.L.C. Rowsell, V. Pralong and L.F. Nazar

“A new class of materials for lithium-ion batteries: iron(III) borates”
J.L.C. Rowsell, J. Gaubicher and L.F. Nazar

“Synthesis, structure, and solid-state electrochemical properties of Cr$_3$BO$_6$:…”
J.L.C. Rowsell and L.F. Nazar
J. Mater. Chem., 11, 3228 (2001)

“Speciation and thermal transformation in alumina sols: ….”
J. Rowsell and L.F. Nazar
Early days of MOFs

Minireviews

Microporous Materials

Strategies for Hydrogen Storage in Metal–Organic Frameworks
Jesse L. C. Rowsell and Omar M. Yaghi

Keywords:
adsorption - hydrogen - metal-organic frameworks - microporous materials - organic-inorganic hybrid composites

Gas Adsorption Sites in a Large-Pore Metal-Organic Framework
Jesse L. C. Rowsell,¹ Elinor C. Spencer,² Juergen Eckert,³,4 Judith A. K. Howard,² Omar M. Yaghi¹

The primary adsorption sites for Ar and N₂ within metal-organic framework-5, a cubic structure composed of Zn₄O(CO₂)₁₂ units and phenylene links defining large pores 12 and 15 angstroms in diameter, have been identified by single-crystal x-ray diffraction. Refinement of data collected between 293 and 30 kelvin revealed a total of eight symmetry-independent adsorption sites. Five of these are sites on the zinc oxide unit and the organic link; the remaining three sites form a second layer in the pores. The structural integrity and high symmetry of the framework are retained throughout, with negligible changes resulting from gas adsorption.

Fig. 3. At 30 K, eight symmetry-independent sites are crystallographically identified as partially occupied by Ar atoms (shown as yellow spheres) in the pores of MOF-5. These include (A to C) three sites primarily associated with the secondary building unit and those above the (D) face and (E) edges of the linker. Sites are labeled according to the description in the text. (F) Sites φ (orange spheres) and η (brown spheres) form a second layer in the large pore above site δ(C₆) (yellow spheres); (G) site 0 (brown sphere) is located at the center of the small pore surrounded by site ε(CH₂)₂ (yellow spheres).
DRIFTS instrumentation

FitzGerald et al., Rev. Sci. Inst., 2006
H₂···H₂ Interactions in MOF-5

Absorbance

Frequency (cm⁻¹)

0.7 H₂ per cluster
1.3 H₂ per cluster
2.0 H₂ per cluster
2.7 H₂ per cluster
4.0 H₂ per cluster

α(CO₂)₃
Infrared Spectrum of $\text{H}_2$ in Mg-MOF-74

FitzGerald et al., JACS, 2011
Band intensities plateau as sites fill

Liu et al., Langmuir, 2008

FitzGerald et al., JACS, 2011
Metal-specific band redshifts

The diagram illustrates the absorbance spectra of various metal compounds across different frequency regions. The spectra are labeled for Q-region, S(0)-region, and S(1)-region. Specific compounds include Ni$_2$L ($2\times$), Co$_2$L, Mn$_2$L, Mg$_2$L, and Zn$_2$L. The absorbance is measured in arbitrary units, as indicated by the scale on the left side of the graph.
High surface area and $Z'$ in a thermally stable 8-fold polycatenated hydrogen-bonded framework†‡

Cassandra A. Zentner,*a Holden W. H. Lai,a Joshua T. Greenfield,a Ren A. Wiscons,a Matthias Zeller,b Charles F. Campana,c Orhan Talu,d Stephen A. FitzGerald*e and Jesse L. C. Rowsell*a

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Accepted 15th June 2015
Predict the crystal packing of this molecule...
Predict the crystal packing of this molecule...
Predict the crystal packing of this molecule...
Predict the crystal packing of this molecule...
Predict the crystal packing of this molecule...
A starting model?
You might have guessed hexagonal
Single crystals after evaporation of ethanol
Large unit cells, twinning, poor resolution
# Crystal data

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space Group</td>
<td>I 2</td>
</tr>
<tr>
<td>Cell Parameters</td>
<td>( a = 31.419(6) \text{ Å} ), ( \alpha = 90^\circ )</td>
</tr>
<tr>
<td></td>
<td>( b = 30.116(6) \text{ Å} ), ( \beta = 90.412(2)^\circ )</td>
</tr>
<tr>
<td></td>
<td>( c = 45.320(9) \text{ Å} ), ( \gamma = 90^\circ )</td>
</tr>
<tr>
<td>Cell Volume</td>
<td>42 880(14) \text{ Å}³</td>
</tr>
<tr>
<td>( Z, Z' )</td>
<td>56, 14 [462 independent non-H atoms]</td>
</tr>
<tr>
<td>Radiation</td>
<td>Mo K( \alpha ), Incoatec ( \mu )S microfocus source</td>
</tr>
<tr>
<td>Temperature</td>
<td>100 K</td>
</tr>
<tr>
<td>Structure Solution</td>
<td>SHELXD</td>
</tr>
<tr>
<td>Reflections</td>
<td>246 105 total, 49 674 unique, 27 787 ((I &gt; 2\sigma[I]))</td>
</tr>
<tr>
<td>Completeness</td>
<td>98.7% to ( \theta = 27.53^\circ )</td>
</tr>
<tr>
<td>Parameters, Restraints</td>
<td>4201, 1</td>
</tr>
<tr>
<td>( R_1(\text{obs,all}) / wR_2(\text{obs,all}) )</td>
<td>0.0875, 0.158 / 0.268, 0.330</td>
</tr>
</tbody>
</table>

Matthias Zeller, Youngstown State University
Charles Campana, Bruker Madison, WI
Stacking of hexagonal sheets
Catenation of non-parallel layers
Remaining void volume is substantial

38% void volume, could be occupied by 167 ethanol molecules, SQUEEZE identifies 1540 e⁻ (45 ethanol)
Crystal structure retained after desolvation
Reversible (de)solvation

![Graph showing intensity vs. 2θ for Cu Kα radiation at different temperatures and conditions.](image)
Bulk crystallization from THF/H$_2$O

50/50 Mixture of water and tetrahydrofuran

1. Heat at 70 °C for 4 h
2. Cool to RT for 10 h
3. Cool to 4 °C for 48 h
4. Agitate

5.
Gas adsorption confirms microporosity

Initial Isosteric Heat $H_2 = -5.7 \text{ kJ/mol}$

Initial Isosteric Heat $CO_2 = -22 \text{ kJ/mol}$

BET surface area 1100 m$^2$/g

Orhan Talu, Cleveland State University
Binding energy trend for H$_2$
tcpb derivatives

\[
\begin{array}{ccccc}
R^1 & R^2 & R^3 & R^4 \\
H & H & H & H \\
H & H & CH_3 & H \\
H & H & OCH_3 & H \\
H & CH_3 & OCH_3 & H \\
H & H & NH_2 & H \\
H & CH_3 & NH_2 & H \\
H & NH_2 & NH_2 & H \\
H & H & NO_2 & H \\
CH_3 & CH_3 & CH_3 & H \\
H & H & H & CH_3 \\
\end{array}
\]
Derivative synthesis

The first step was performed under nitrogen atmosphere for all of the compounds.

The second step, hydrolysis of the methyl esters, was performed under nitrogen atmosphere.
Derivative synthesis

The first step was performed under nitrogen atmosphere for all of the compounds.

The second step, hydrolysis of the methyl esters, was performed under nitrogen atmosphere.
Comparison of local structure

tcpb
8-fold catenation
Comparison of local structure

tcpb-CH$_3$
7-fold catenation, methyls concealed
tcpb derivatives

<table>
<thead>
<tr>
<th>R¹</th>
<th>R²</th>
<th>R³</th>
<th>R⁴</th>
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<tbody>
<tr>
<td>H</td>
<td>H</td>
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<td>H</td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>CH₃</td>
<td>H</td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>OCH₃</td>
<td>H</td>
</tr>
<tr>
<td>H</td>
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<td>H</td>
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<tr>
<td>H</td>
<td>H</td>
<td>H</td>
<td>CH₃</td>
</tr>
</tbody>
</table>
tcpb-NO$_2$ synthesis
Comparison of local structure

tcpb-NO$_2$
7-fold catenation,
some NO$_2$ exposed
Oberlin student coauthors on our papers

Kelty Allen
UC Berkeley

Jesse Hopkins
Cornell

Patrick Landreman
Stanford

John Matters
O.C.S.

Ross Myers
Columbia

Brian Burkholder
U. Washington

Michael Friedman
Boston U.

Josh Greenfield
UC Davis

Jenny Schloss
M.I.T.

Chris Pierce
Ohio State

Elizabeth Gilmour
U. Memphis

Jocienne Nelson
Cornell
Student leaders on tcpb paper

Cassandra Zentner
Oberlin → ?

Ren Wiscons
U. Michigan

Holden Lai
U.C. Berkeley
Core functionalization: pyrylium intermediate
Core functionalization: Suzuki coupling

Br
Br
Br
Br
X
+ 1. Pd°
2. NaOH
MeOOC

COOH

HOOC

COOH
Smaller IR band redshifts for adsorbed H$_2$