Making a Silk Purse out of a Sow’s Ear

Publishing Difficult Data

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A Chemical Crystallography Service

- “Just crystal Structures”
- Support for research
- Support for manuscripts
- Minimal involvement in “the Science”
- “Routine”

“Stamp Collecting”
Increased Automation

**User**
- Choose and mount crystal
- Start screening image collection
- Start the data collection
- Publish the result

**Automation**
- Index the data
- Determine the Laue class
- Decide the acquisition time
- Decide the strategy
- Integrate the data
- Determine the space group
- Solve and refine the structure
Image Inspection

$\text{PEG}_{16}$

Ferrocene Macrocycle

Poor Structure or Poor Data?

$\lambda_{\text{max}} = 976$ nm

Davis et al., *Org. Lett.*, 2010, 12, 2124
Poor Structure or Poor Data?

Davis et al., Org. Lett., 2010, 12, 2124
Barluenga’s Reagent

- Justin Chalker & Ben Davis (February 2009)
  - A safer, better synthesis
  - “It’s a known structure, we just want to confirm that it’s the same...”

Barluenga’s Reagent

250 K
a = 12.3206 Å
b = 7.9297 Å
c = 14.7047 Å
β = 113.290°

150 K
a = 12.1662 Å
b = 15.7653 Å
c = 14.6030 Å
β = 113.489°
Barluenga’s Reagent
Barluengaga’s Reagent

Graph showing the relative temperature to 300 K against temperature in K for three different curves (a, b, and c).
Barluenga’s Reagent
Barluengoa’s Reagent

\[ K_{im}, \quad M_{K_{in}} \quad C_{r} \quad G_{ro} \quad D_{e}, \quad 2014, \quad 14, \quad 6294-6301. \]
Barluengas’s Reagent Derivatives

Barluenga’s Reagent Derivatives

\[
\begin{align*}
\text{[Structural formula 1]} & \quad \text{[Structural formula 2]} \\
\text{[Structural formula 3]} & \quad \text{[Structural formula 4]}
\end{align*}
\]
## Barluenga’s Reagent Derivatives

<table>
<thead>
<tr>
<th></th>
<th>Polymorph I</th>
<th>Polymorph II</th>
</tr>
</thead>
<tbody>
<tr>
<td>I(Coll)$_2$ClO$_4$ (BAZNAR)</td>
<td>Br(Coll)$_2$ClO$_4$ (AKOXON)</td>
<td>I(Coll)$_2$ClO$_4$</td>
</tr>
<tr>
<td>$a$/Å</td>
<td>27.844(5)</td>
<td>27.280(30)</td>
</tr>
<tr>
<td>$b$/Å</td>
<td>11.036(2)</td>
<td>11.028(11)</td>
</tr>
<tr>
<td>$c$/Å</td>
<td>23.412(7)</td>
<td>23.551(20)</td>
</tr>
<tr>
<td>$\beta$/°</td>
<td>126.47(2)</td>
<td>127.19(1)</td>
</tr>
<tr>
<td>Volume /Å</td>
<td>5785.7</td>
<td>5644(9)</td>
</tr>
<tr>
<td>Space Group</td>
<td>C2/c</td>
<td>C2/c</td>
</tr>
</tbody>
</table>

A flat half molecule & a twisted whole cation

2 half cations both flat
## Barluenga’s Reagent Derivatives

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<tbody>
<tr>
<td>Br(Coll)$_2$ClO$_4$</td>
<td>Br(Coll)$_2$ClO$_4$</td>
<td>And Br(Coll)$_2$BF$_4$</td>
</tr>
</tbody>
</table>
Cooling to 30 K

- Data at 30 K at Diamond
  - No diffuse or satellites

- Crystal at home
  - Diffuse features

- Same crystal at Diamond, at 100 K 24hrs later
  - No diffuse or satellites...
Radiation Damage

- Repeatedly collect same measurement on the same crystal
- 45° phi scan
- 45 seconds of exposure per scan
- Look for change in peaks

Scan 1

hk1 plane
4.0 Å

Mo, Mg, K, m, Ca, C, Co, m.
Radiation Damage

- Repeatedly collect same measurement on the same crystal

- 45° phi scan

- 45 seconds of exposure per scan

- Look for change in peaks
Radiation Damage

- Repeatedly collect same measurement on the same crystal
- 45° phi scan
- 45 seconds of exposure per scan
- Look for change in peaks

Scan 3

Radiation Damage

- Repeatedly collect same measurement on the same crystal
- 45° phi scan
- 45 seconds of exposure per scan
- Look for change in peaks

The Silk Purse...?
If the Structure is Known to be wrong...

Fleming, et al., manuscript in preparation.
If the Structure is Known to be wrong...

- Diffuse scattering ✓
- Uncertain (pseudo)symmetry ✓
- Twinning ✓
- Modulation (✓)
If the Structure is Known to be wrong...

- Diffuse scattering ✓
- Uncertain (pseudo)symmetry ✓
- Twinning ✓
- Modulation (✓)

Still useful...
If the Structure is Known to be wrong...

- Diffuse scattering ✓
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- Still useful...
If the Structure is Known to be wrong...

- Diffuse scattering ✓
- Uncertain (pseudo)symmetry ✓
- Twinning ✓
- Modulation (✓)

- Still useful...
Publishing Difficult Data?

• “Real science” not “just a crystal structure”
• Use the ESI and include
  • Description/Discussion
  • Selected raw images
  • Reconstructed reciprocal lattice sections

• Raw data?
• A crystal structure is just a model...
The Other Little Piggies...

- Kirsten Christensen
  - Emma McKinley
  - Yejin Kim
  - Lewis Morgan
  - Georgia Scurfield
  - Tora Flemming
- Nick Funnel (ISIS)
- Claire Murray (II1, DLS)

- Alasdair French, Justin Chalker & Ben Davis
- Nick Evans, Chris Serpell & Paul Beer
- Nicola Davis & Harry Anderson