CRYSTALS workshops

"twins"

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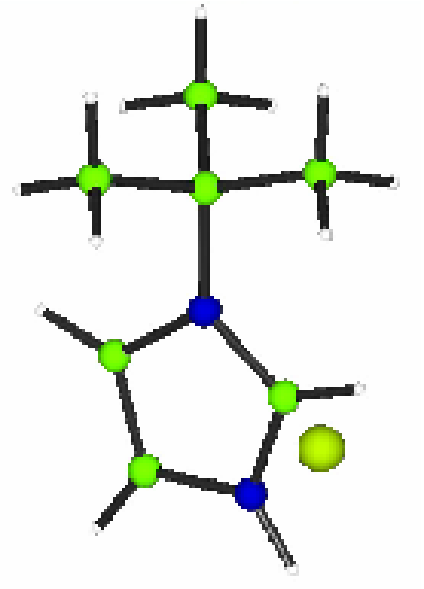

Keen ($C_7H_{13}ClN_2$): Pseudo-merohdral twin

Summary

This data for this material were collected by on a Nonius KappaCCD diffractometer with Mo Kα radiation.

Expected Formula C_7 H_{13} Cl N_2. Temperature 150K
Monoclinic b unique

- The structure was solved with 2 molecules in the asymmetric unit in $P2_1$ but failed to refine to an R-factor below 30%.
- Using the systematic *weaknesses* as a guide, it was postulated that the sample was a poor quality in P 2_1/c. The structure again solved in this space group, but failed to refine below 20%.
- Finally, it was recognised that the material was twinned. The R factor fell to below 3%, with all the hydrogen atoms showing in a difference map.

First Attempt (for your information only):

Importing and solving using the space group P 2_1 gives a reasonable structure with two independent molecules, but it fails to refine.
SIR92 leaves a diagnostic file in the working folder. CAMERON can also be used to get a global view of the structure.

Tools at your disposal:
You could open *SIR92.lis*. Type: **$notepad sir92.lis**

The volume per atom looks OK, there is no translational pseudo-symmetry, but all the statistics point strongly to acentric. This is unusual (but not impossible) for a synthetic material.

You could use **CAMERON** to look along the *b* axis at a '**complete**' packing diagram. The two independent molecules might be related by a *c* glide. To do this you would:
Click **Cameron** on the toolbar. Change selection from **Unpack** to **Complete**. Click the button **Axis b**. Close Cameron window. **Do not** apply changes made in Cameron.

Second Attempt (for you to try):

If you have tried the **First Attempt**, navigate to the **Keen** folder and delete the **crfilev2.dsc** file. Import the data (*keen.ins, keen.hkl*), trying space group **P 1 2_1/c 1**. Follow the same steps as for the other structures, but take note of the statistics for the systematic absences, and for the merging R factor.
The structure should solve in Sir 92. **Delete the spurious C peaks, *but be careful not to delete the Cl anion!***
You will find that it still fails to refine to a decent R-factor.

Diagnosis:

Scroll backup up the text page until you find the reflection input section.

- The mean value for the systematic absences is unusually high (it is almost always greater than zero).
- R_{int} is good, especially for the medium and strong reflections.

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Centro-symmetric space-group.
* Friedel Pairs will be merged.
* Removing systematically absent reflections
   119 absences,    mean Fo =   23.090    rms Fo/sigma(Fo)=  24.535

Fo range          -ve    1.000    2.000    4.000    8.000   16.000  Remainder
Mean Fo        -3.675    0.000    1.620    3.166    5.384   12.344   59.662
Number             29        0        6       17       17        6       44

Fo/sigma range    -ve    1.000    2.000    4.000    8.000   16.000  Remainder
rms (Fo/sigma)   1.991    0.581    1.370    2.828    5.875   12.295   44.714
Number             29       14       14        9       11        7       35

  3794 reflections accepted              119 reflections rejected

 2016 merged reflections output          0 merged reflections rejected
 1857 Reflections greater than 3 sigma(i),  92.113 percent of data
Rint = [Sum(/Fsq-<Fsq>/)/sum(Fsq)]                    =  0.018
Rmerge    = SQRT[ sum[w(Fsq-<Fsq>)**2] / sum[w<Fsq>**2]] =  0.013
Rint for I>10sigma,  10sigma>I>2sigma,    I<2sigma
          0.015           0.074           0.858
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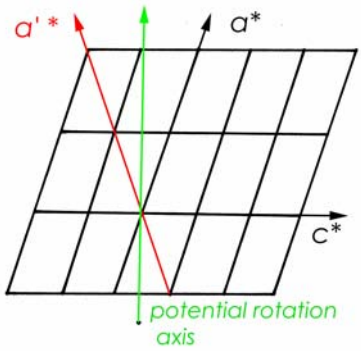
- Look at the systematic absences plot

Start worrying about the crystal being twinned. A scale drawing of the reciprocal lattice shows the possibility of a pseudo-orthorhombic super-cell (in red).

Reciprocal Lattice for a centred pseudo-orthorhombic cell, Beta=91.

The pseudo-orthorhombic super lattice means that twinning is possible by rotation about either c^* or a.



Rotation of the whole lattice about either axis does not result in exact overlap of reciprocal lattice points - this type of twining is termed pseudo-merohedral (TLQS) twinning. However, the almost orthorhombic β angle of 91.13 degrees means that in practice both lattices overlap, so that every observation contains contributions from both twin domains.

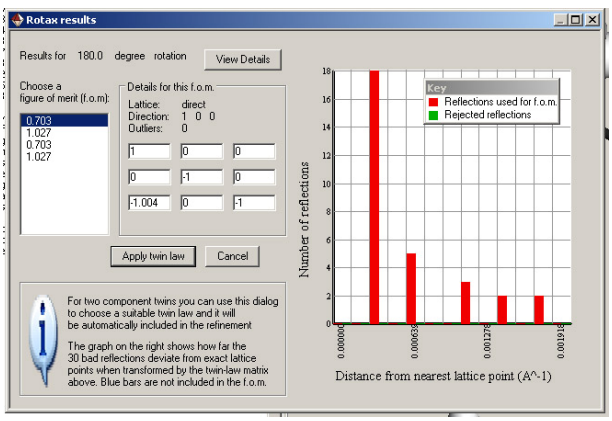
This type of twinning is easily treated in CRYSTALS – once the twin law is identified. From the diagram we propose a rotation of 180 degrees about *c**, which transforms the indices as:

$$h' = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 1 & 0 & 1 \end{bmatrix} . h$$

ROTAX will do this for you.

Twinned Refinement: Easy

Guided treatment of two-component merohedral and pseudo-merohedral twins is implemented in the CRYSTALS GUI: Choose
GUIDE > Analyse > Rotax Analysis > ROTAX



Select a low "fom" twin law and apply it.
Use the GUIDE to set up a refinement. Note that the twin elements are now automatically included.

The R-factor should drop very quickly, and at the end of the guided refinement should end up below 3%