**X-ray Crystallography 12650 - CHM 69600-006**

***Homework Assignment 8:***

***A carborane salt with C/B substitutional disorder and twinning***

*Questions are 5, 20 or 50 points, as indicated. Due date: One week after assignment.*

1) Download the compressed folder “homework 8” from the class web page. Determine the space group using XPREP and solve the structure using direct or Patterson methods. With the help of the synthesis layout (below), assign all non-H atoms and refine the structure.



Once all non-H atoms are assigned, continue with anisotropic refinement, rename atoms in a meaningful way, sort the atoms, and update the weighting scheme multiple times until it does not change any more.

At this point, check if the refined R values are as expected. Are they e.g. much larger than expected based on the data R values (Rint and R sig). A possible cause for this can be twinning.

Use the program **Platon** to check for possible twinning.

Platon needs a different data format that we usually use to check for twinning. Add the command ACTA and change the command “LIST 6” to “LIST 4” and run a refinement cycle (this eliminates the difference density maps, but allows to check for twinning).

Open the program Platon. Open your cif file (“File”, then “Select Data File”). Open the graphical interface (“Start”, then “Graphical Menu”). In the “Symmetry Column”, click “TwinRotMat”.

Inspect the suggested possible twin laws and twin transformation matrices. Look for twofold rotations around a low index axis that feature a transformation matrix with values limited to 0, 0.5, 1, 1.5 and 2 (some rounding allowed). Write down possible transformation matrices. Make a screen shot of the page, then close all Platon windows.

In Shelxle add a line TWIN, followed by the nine numbers of the transformation matrix. Add a line BASF, followed by a number close to zero (e.g. 0.1, this is the fraction of the minor twin component and will refine). Run a few refinement cycles.

If the structure is indeed twinned by the transformation chosen, then the R values should drop, and difference density values should become smaller. The BASF value should be different from zero. If this is not the case, try another matrix suggested by Platon until you found the correct one.

Twinning can often cause the actual symmetry being obscured. Run checkcif to check for missed symmetry, or use Platon to do this. Use the same procedure as for twinning, but choose Addsym instead of TwinRotMat.

If Platon finds possible missed symmetry, you can create a new res file with this symmetry implemented. Click on ADDSYM-SHX (lower right corner). You might have to re-add some items into the new res file (TEMP, SIZE, the twinning commands etc), and you need to rename the res file (ending in \_pl) to match the existing hkl file.

Repeat the above steps as required (rename atoms if needed, etc).

Check for potential disorder. Use the tools of Shelxl and Shelxle for refinement of disorder such as PART or negative PART commands. Depending on the type of disorder, use SAME, SADI, DFIX, and SIMU or ISOR to properly refine all disordered sections of the structure. If necessary, move atoms to meaningful positions using the MOVE and COPY commands of Shelxle (right mouse click). Pay attention to occupancies of disordered atoms. For atoms in exactly the same position, use of EADP or EXYZ might be useful. **Might refinement of more than two-fold disorder be necessary?** Make sure the final result is chemically and physically meaningful before proceeding.

Then place H atoms. Use the automatic HFIX command were possible. For hydrogen atoms that are not automatically assigned this way, choose suitable fitting manual HFIX commands (from the table of “Common HFIX commands” powerpoint slides page 119). If you placed H atoms not using the “automatic HFIX” command of Shelxle, explain your choice of action used.

Check the list of “Most Disagreeable Reflections” in the lst file for reflections that might be obstructed by the beam stop. These would be reflections with very small observed but large calculated intensities at low resolution (i.e. with high values for the resolution in Å). Use “OMIT h k l” lines in the res file to leave these reflections out of the refinement.

Repeat updating the weighting scheme again. Investigate the structure for further changes needed. Are all atom types indeed correct? Are all hydrogen atoms there and placed correctly?

When confident that your model is complete and correct, add missing items to the res file (ACTA, BOND $H, CONF). Check if the formula and Z values are correct. Update or correct them if needed.

Run several refinement cycles again and make sure the weighting scheme is final and that the structure has settled (no large displacements any more). Once finished, run a first checkcif report to check for any oversights or mistakes. Correct as needed and repeat the last steps.

Print out a copy of the res/ins file and hand in with the assignment. Make a screenshot of the Shelxle view with atom labels, print it out and staple it to the res/ins printout. 50 points

2) Fill in the missing items in the CIF. Use the values given below and the instructions in the file “CIF Entries 2017 for Purdue Quest instruments” on the class web page. Pay attention to the Z value, the sum formula and the moiety formula. Prepare a final checkcif report (including structure factor checks) and print out a copy. 5 points

3) Describe the disorder you refined from a chemical and structural point of view (ca 20 lines of text, not focusing on the way it was refined, but what it means for the structure. How would you describe this in a peer reviewed publication?).

Describe the twinning, in your own words (ca. 20 lines of text). Include the screen shot from Platon. What type of twinning is it (merohedric, non-merohedric, or pseudo-merohedric. Explain your choice)? Why is inclusion of the twinning important? 20 points