Olex Tutorial

the full process for solving a small molecule crystal

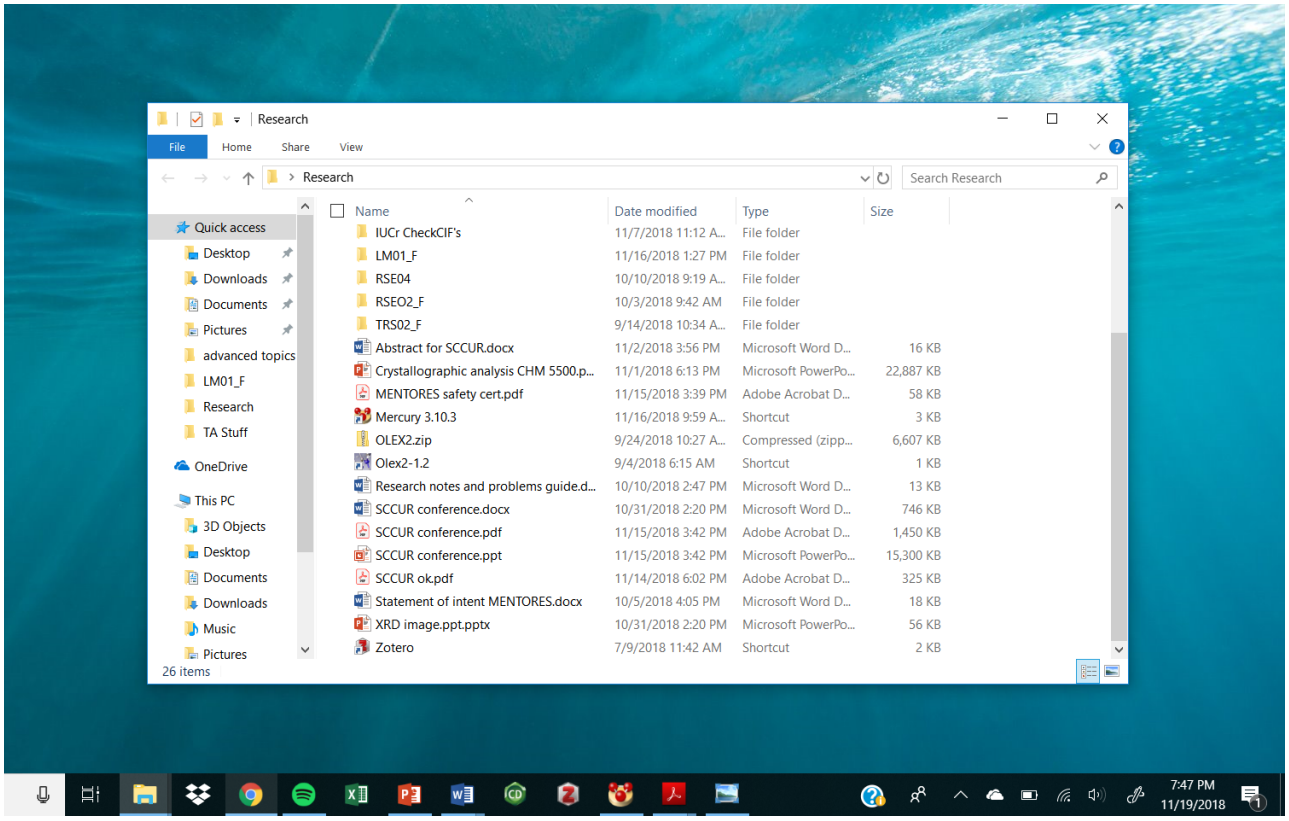
Before starting this tutorial please read the following

I. This tutorial is to familiarize students with the process for solving a crystal
II. All of the files for this tutorial have to be located in the same place in order for the tutorial to work.
III. Students should look at the next step of the tutorial if they are confused on a step before asking for help, this may answer their question.
IV. If clicking refine ever results in an atom that is large or not supposed to be there, delete the atom and refine the system. Then name the q-peak that appears with the proper name if it is an atom that needs to be there. The full structure is seen in step 15.
V. This tutorial needs to have color for the purpose of assigning atoms properly. If printed please print in color, or please give access to an electronic copy.

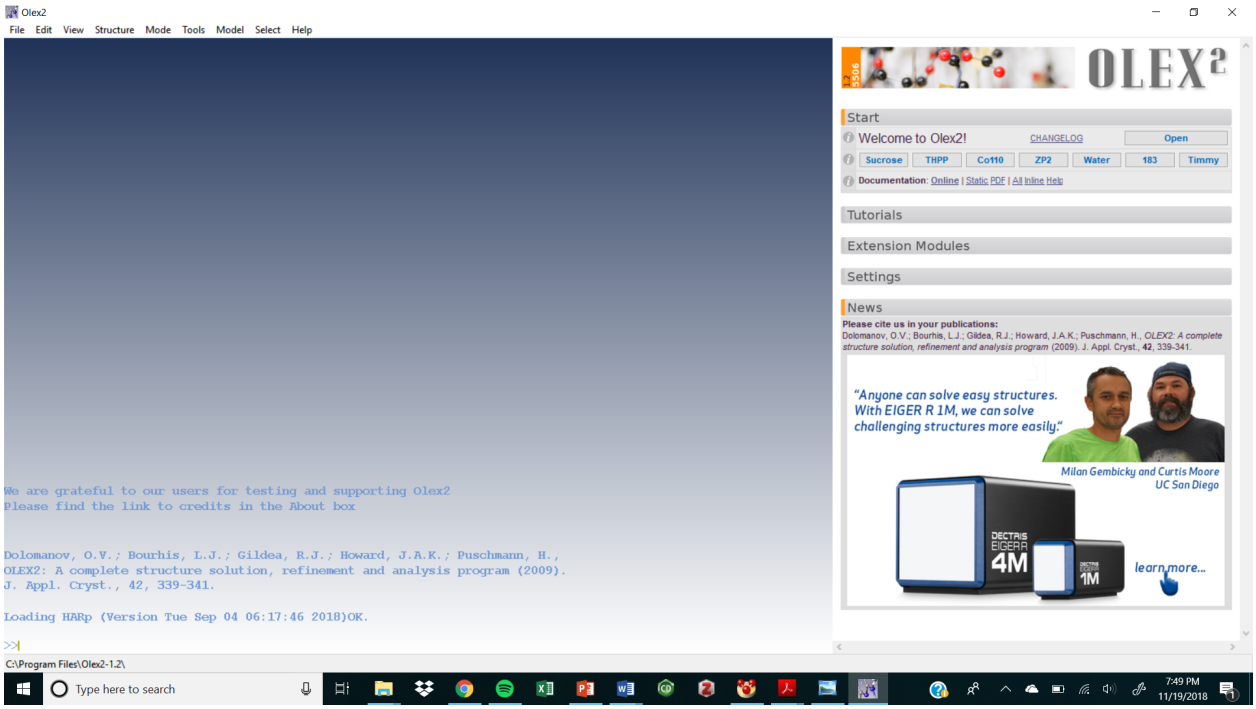
Enjoy and hopefully you will understand how small molecule systems are determined to a publishable quality by the end of this.

Olex^2

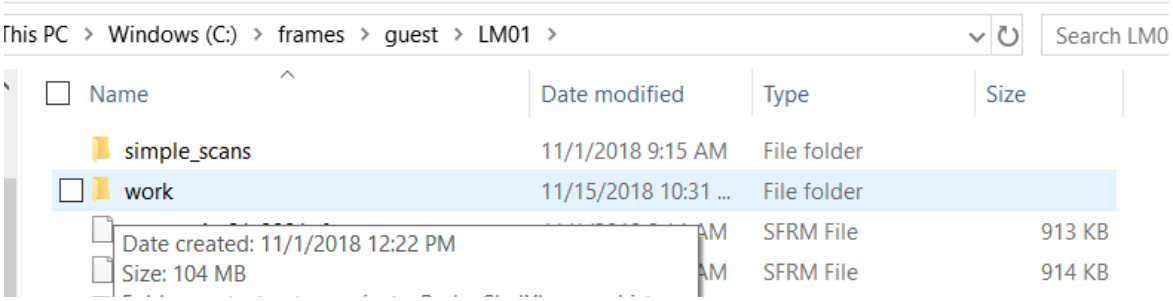
1. Open Olex^2 program labeled “Olex2-1.2”



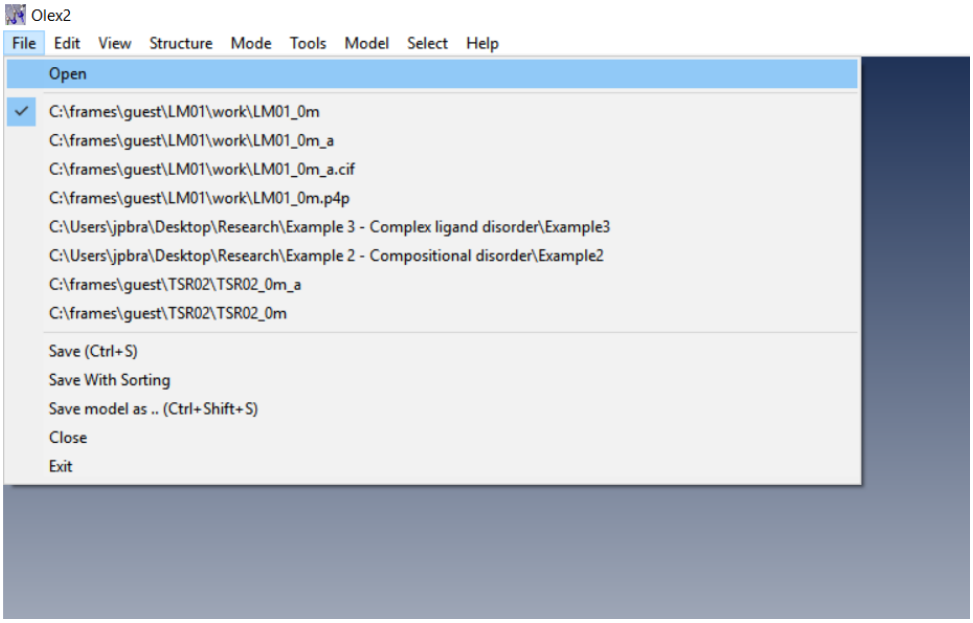
2. Selecting it brings up this page



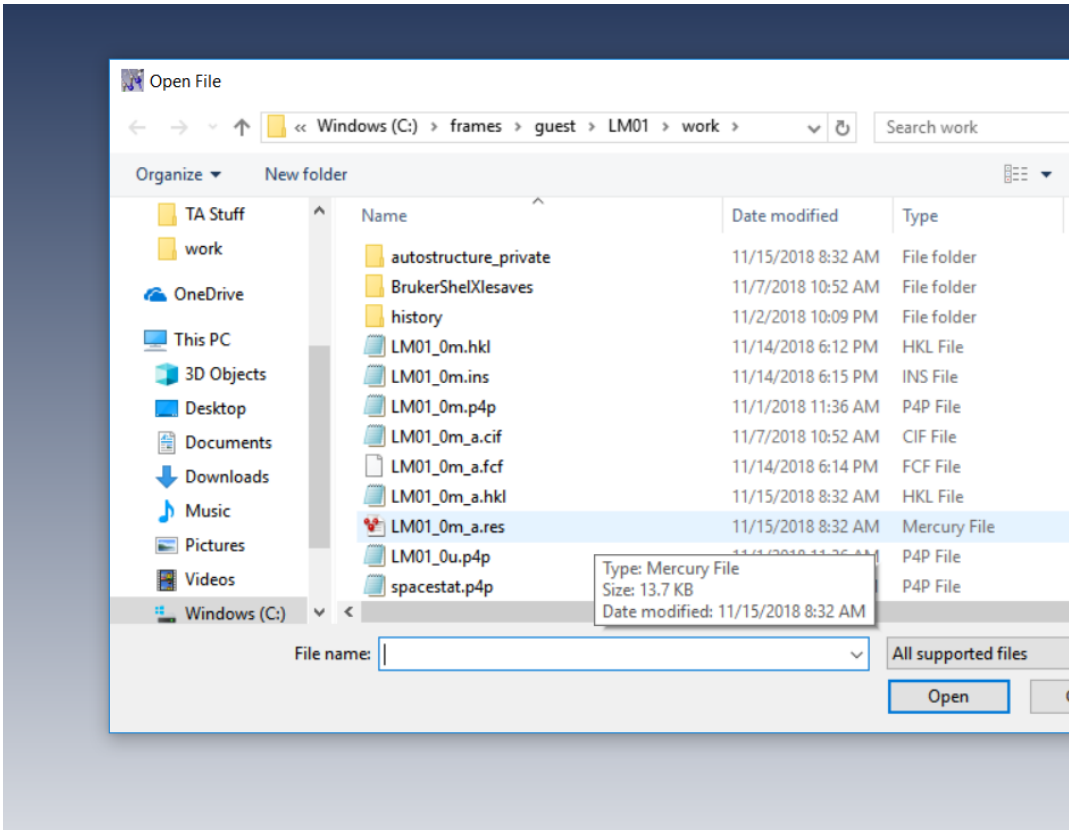
3. Now we must make sure that we have the proper files, all of which should be given to you in a series of downloads and can be found in the download folder.



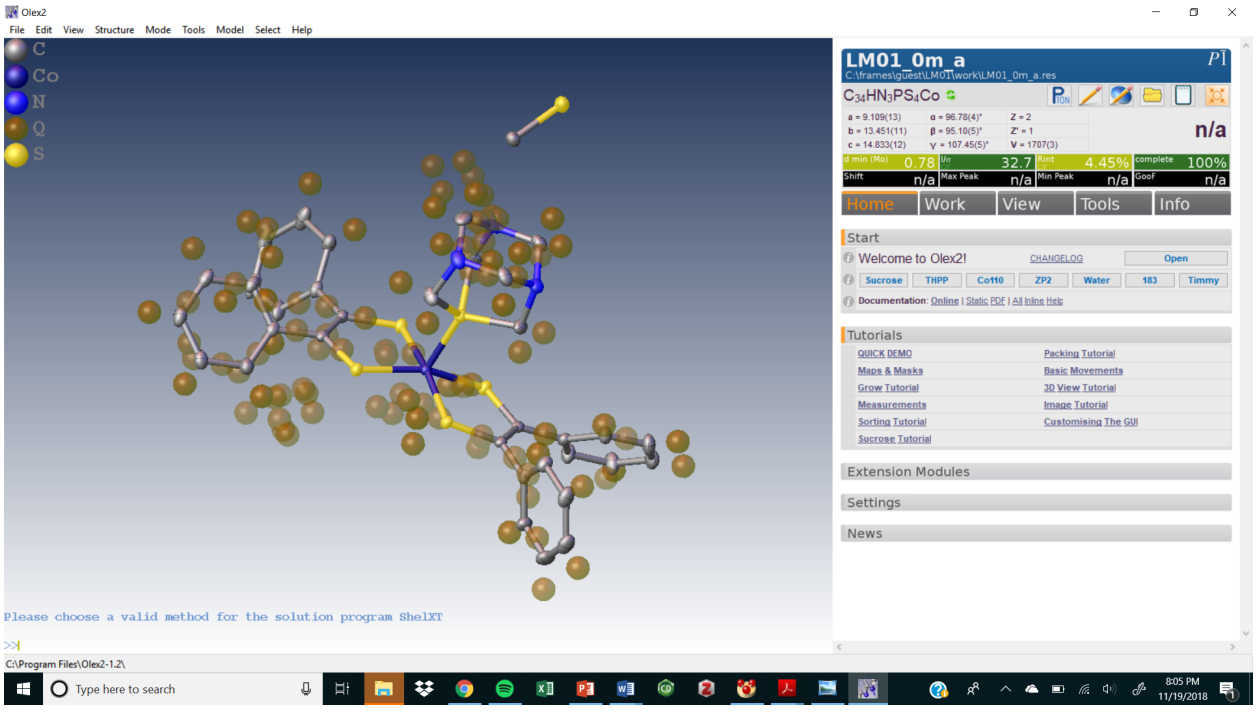
4. Inside of the download folder it should contain the following file types
    a. LM01_0m.hkl
    b. LM01_0m.p4p
    c. LM01_0m.lst
    d. LM01_0m.fcf
    e. Lm01_0m.res
5. After making sure that your files are downloaded properly you can open the structure in Olex by going to
    a. File
        i. Open



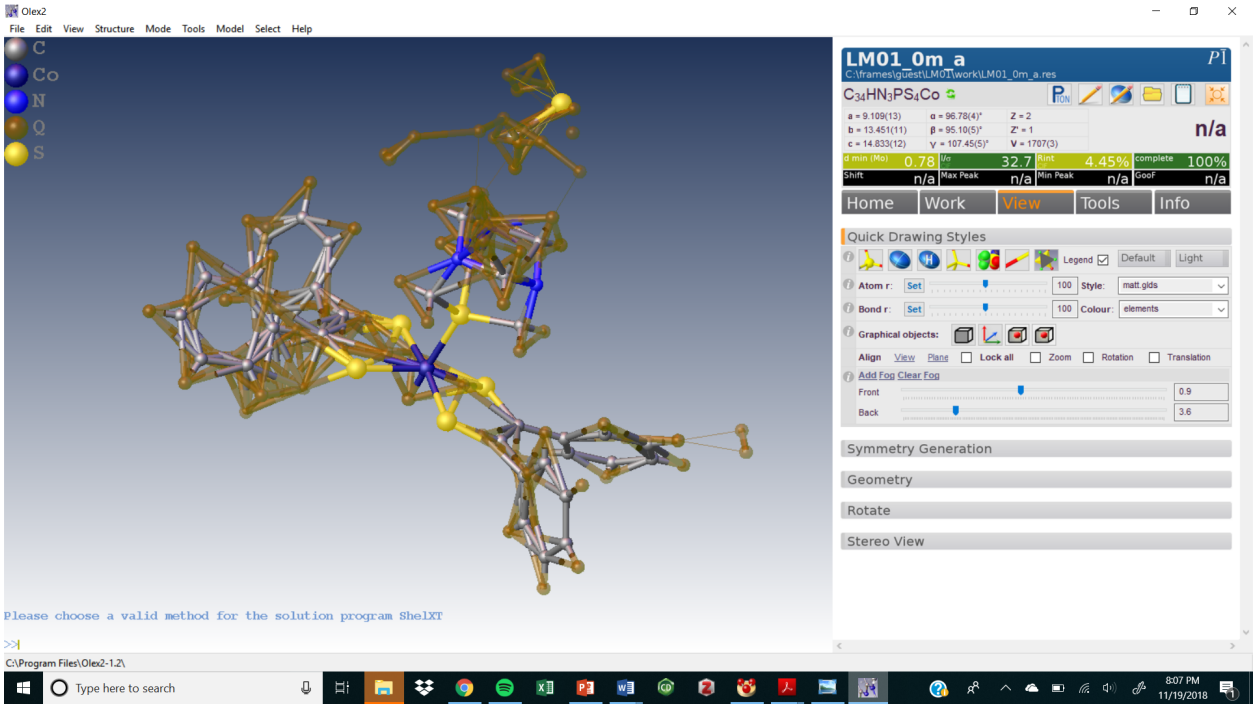
ii. And selecting the RES file in the Work folder



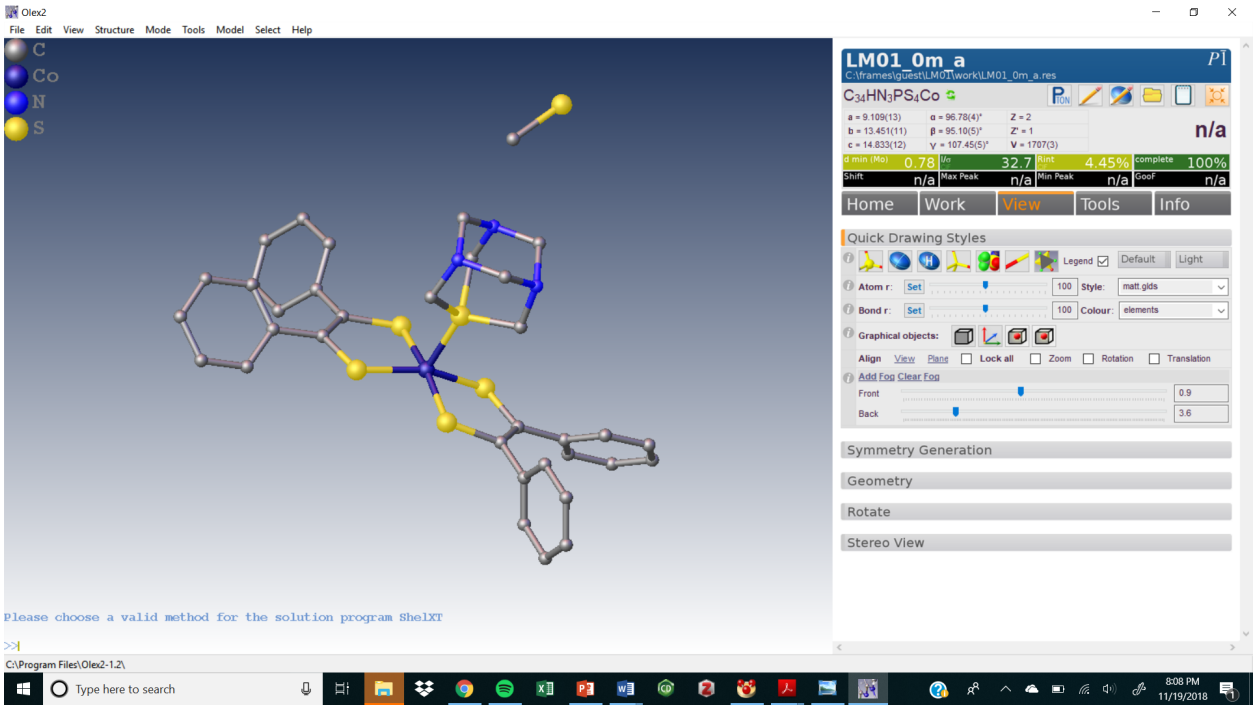
6. Which will give you something like the following screen when you open this file.



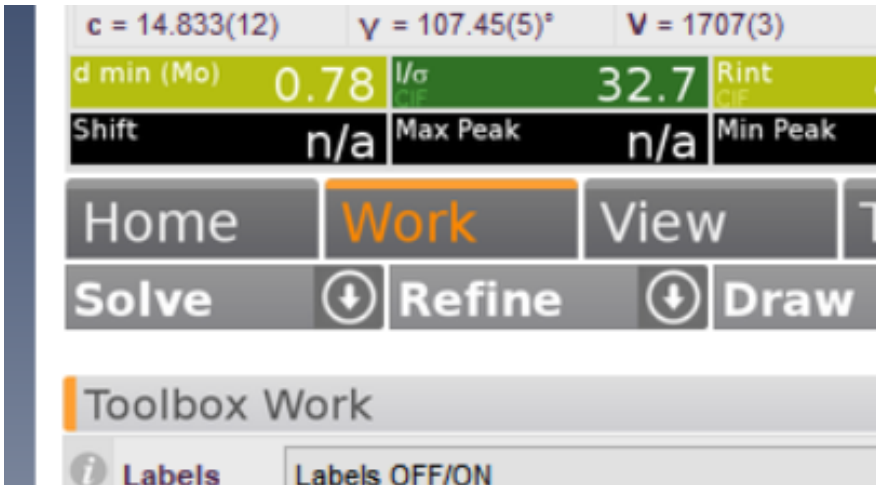
7. To clean up the picture we are going to hide the brown spheres known as Q-Peaks (unassigned electron density). To do this press “control Q.” After pressing once it will show the following screen, for Mac (a two-finger scroll should eliminate them).



8. Repeat this command and it will eliminate the Q-peaks, or continue scrolling to remove them.

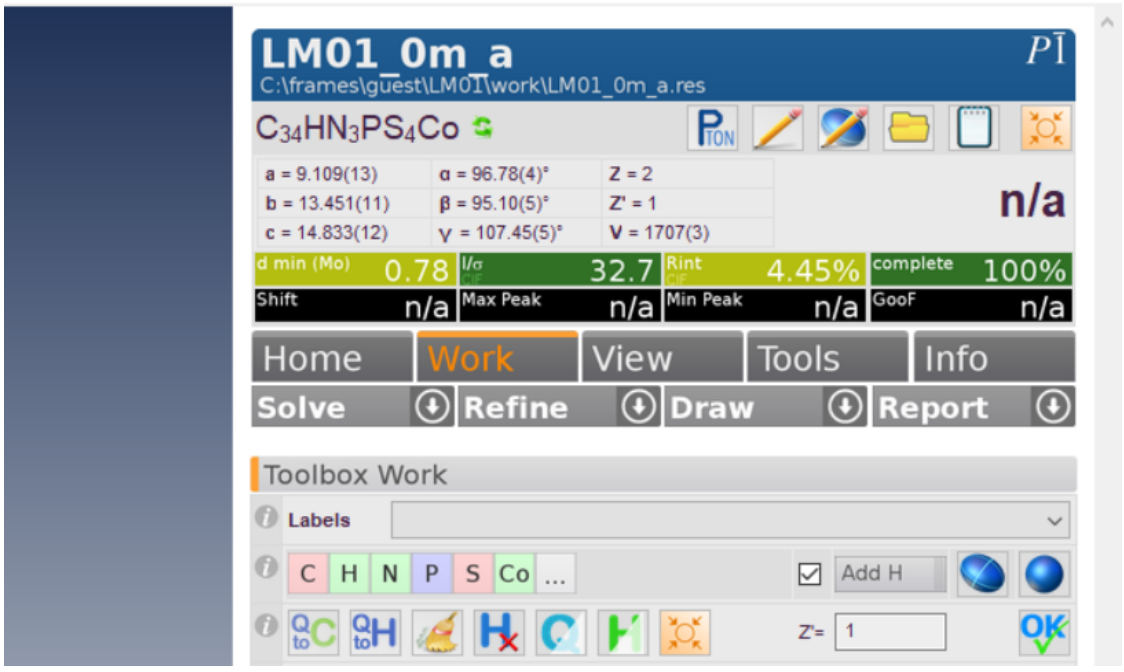


9. go to the “solve” tab under the “work” insert.

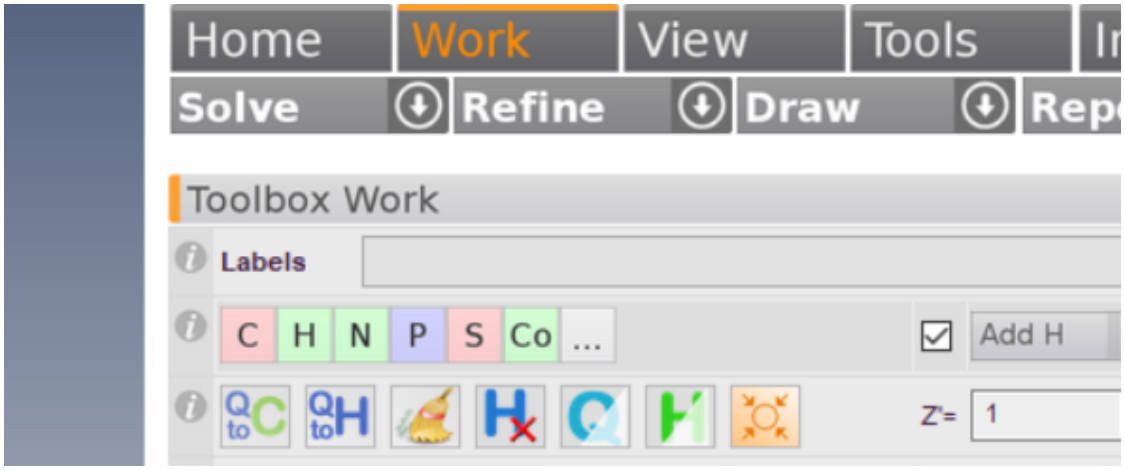


10. Select solve and then select the arrow next to the word solve, you will need to check the assign box and auto box if they are not already selected after you solve the structure. This assigns atoms to the Q-Peaks determined by the solve function.

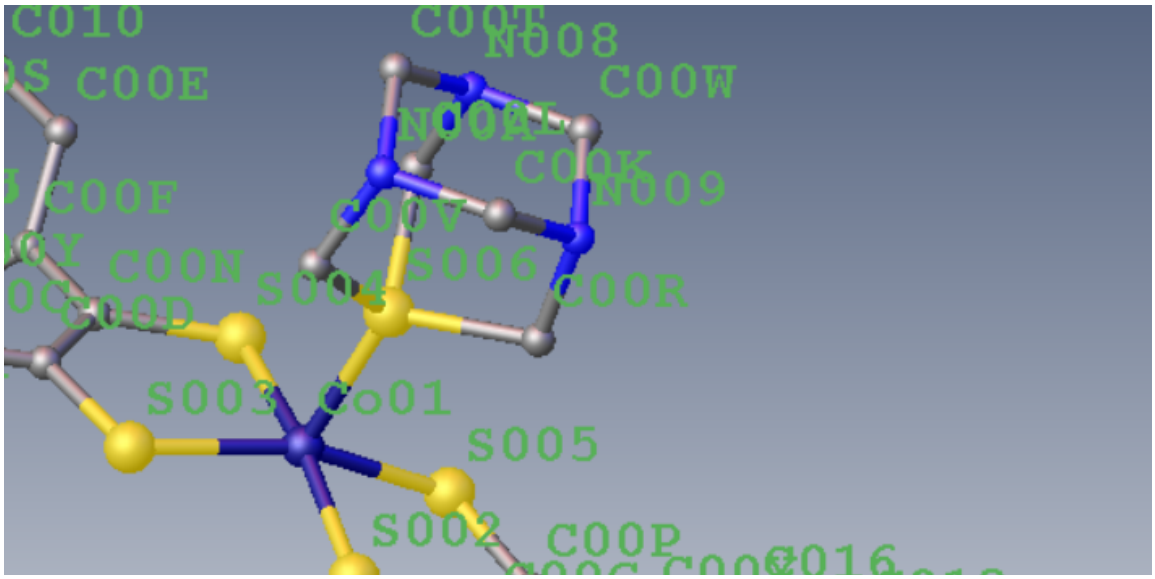
11. Now that the system is solved and cleaned up it is important to know what the chemical formula is. For this sample it is (C35 H37 Co1 S4 N3 P1 Cl1) where the atom type is given followed by the number of atoms of that type. Change the structure to match this formula by changing atoms such as Sulfur, Phosphorus, Nitrogen, and Chlorine by going to the “Work” tab in the sidebar options.



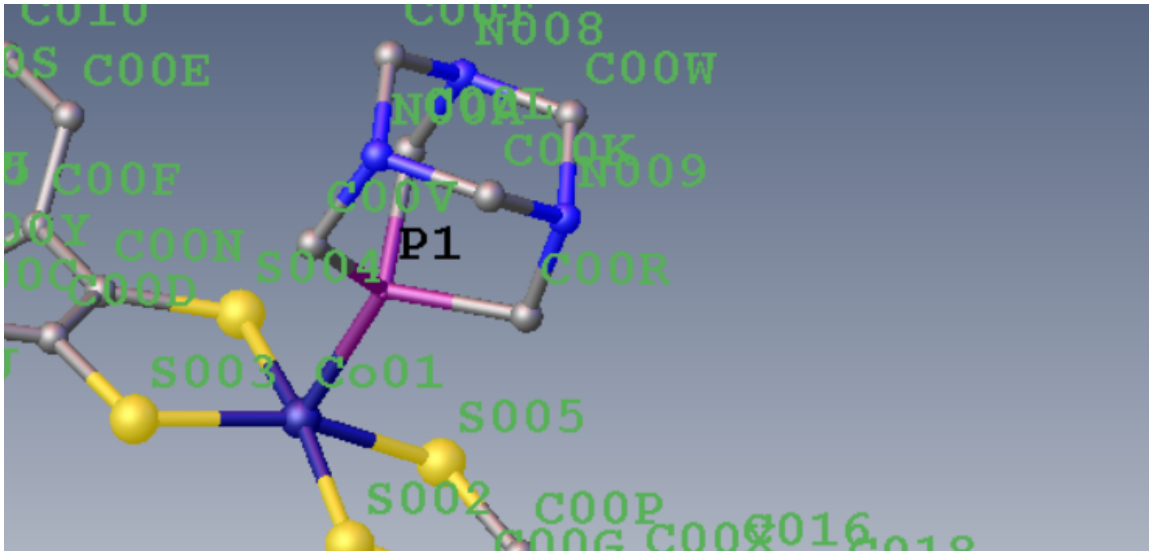
12. Select “P” in the “Toolbox Work” Insert.



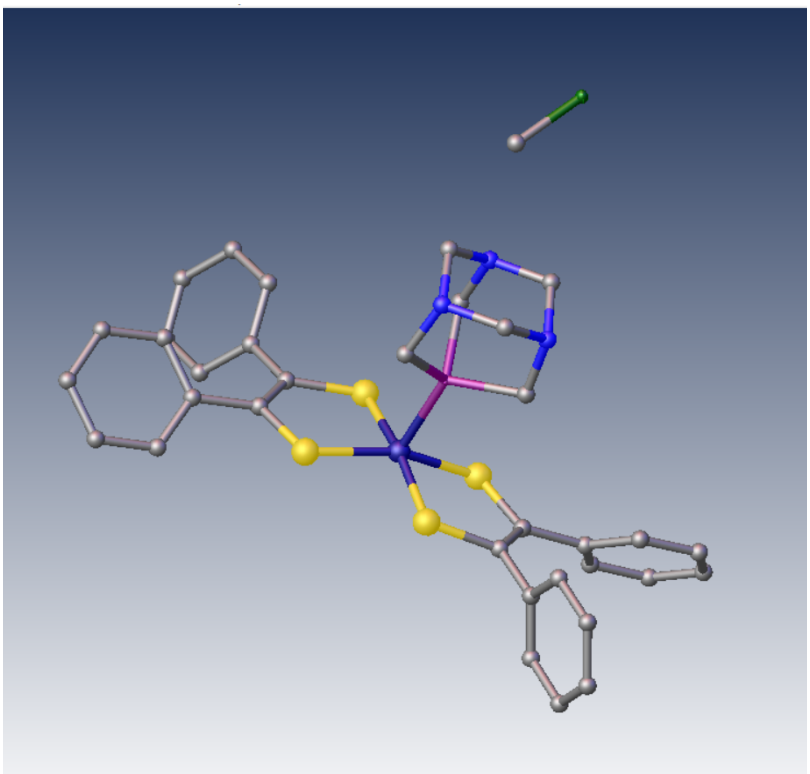
13. Then select the atom in the center above the cobalt core.



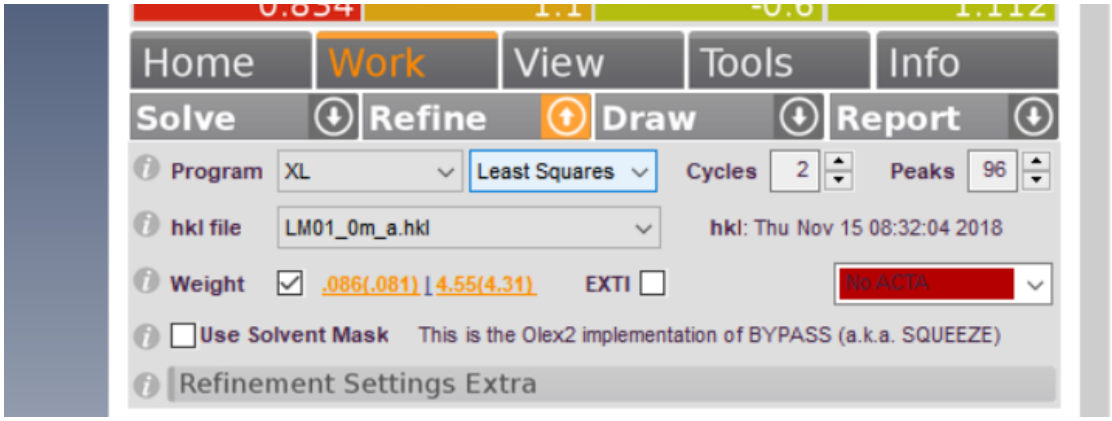
14. It will change sulfur “S006” to a phosphorus “P1” atom as shown.



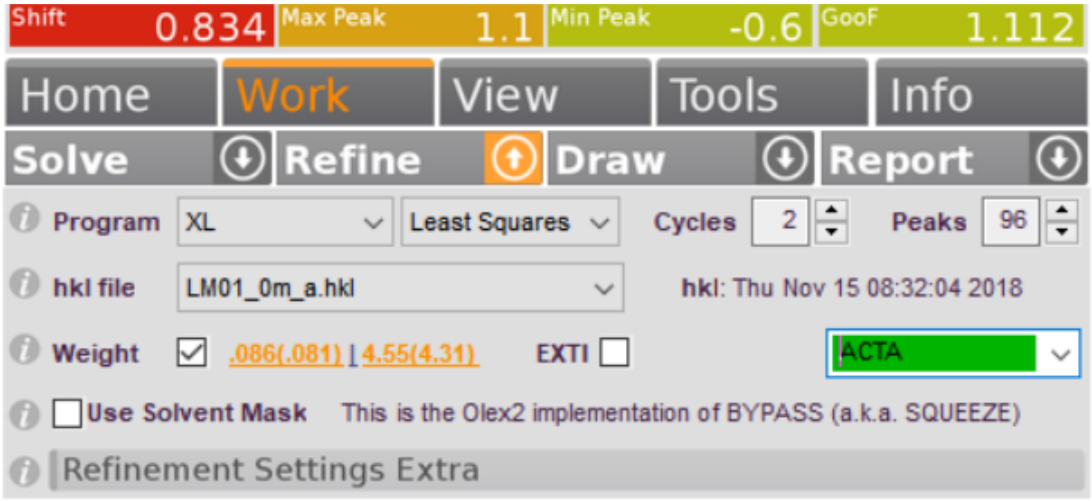
15. Repeat this until the structure has only the number of atoms and the labels that are in the chemical formula (C35 H37 Co1 S4 N3 P1 Cl1) which will result in the following. The solvent may be on the top or bottom of this structure due to the repeating unit cell containing half of the solvent. Depending on the half that is solved it will either be on top or on bottom. Hydrogen atoms are not placed yet so do not worry about them yet. They will be placed later in the tutorial. Make sure not to select a Q peak for the chlorine in the DCE molecule, the solve will automatically place an atom there. If there is a small (almost non-existent) atom that is the chlorine, use shift+click and drag to highlight it then change it to chlorine.



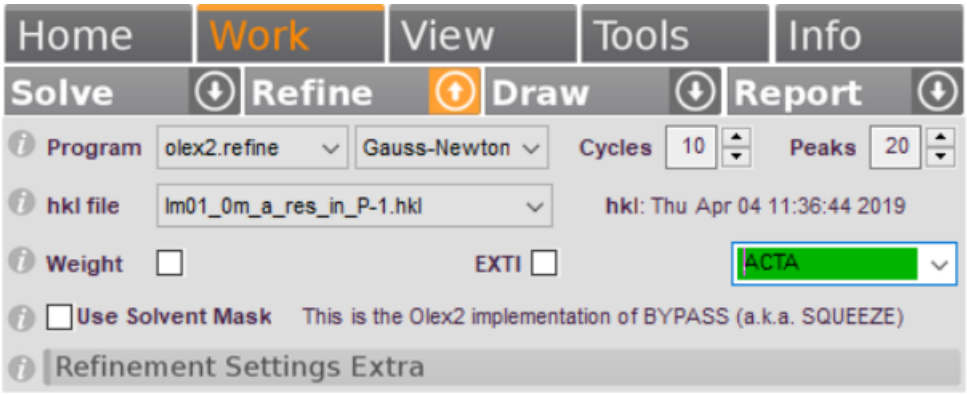
16. After “solving” and “renaming,” go to the “Refine” tab and select the down arrow. To bring up the refine window (your window may not look exactly the same)



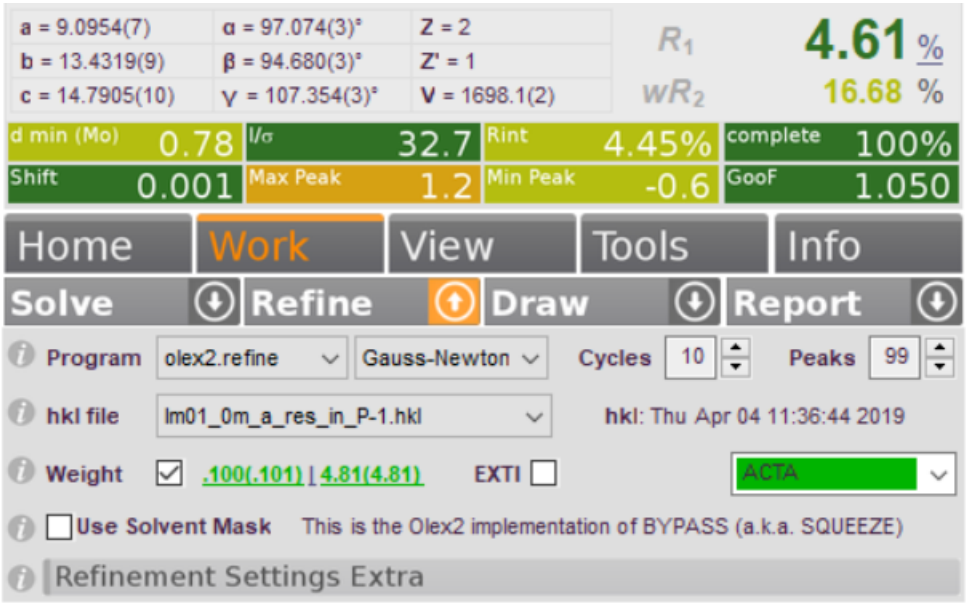
17. Change the selection of “No Acta” to read “Acta” and select the “weight” box.



18. Now change the cycles position to 10, this will cause the refinement to happen 10 times. At this time make sure that the OLEX2.refine is in the program box, and that the GaussNewton method of refinement is chosen in the box next to it.



19. Now click on the refine tab and you should see it processing followed by much better R, wR2, GOOF, and Shift values indicated by colors that are closer to green and further from red. If it is not very close to green just click refine again until the weight numbers are green.
20. An anisotropic refinement (where electron densities are not treated as perfect spheres) will need to be done to get the R_1 value below 5% to perform this select the blue ellipsoid in toolbox right of the add H button. The weight should also be converged this will be indicated by green numbers next to the box checked weight. If these numbers are not present select the checkbox and do another refinement. When the value for R_1 is below 5% then you are done with this refining process.



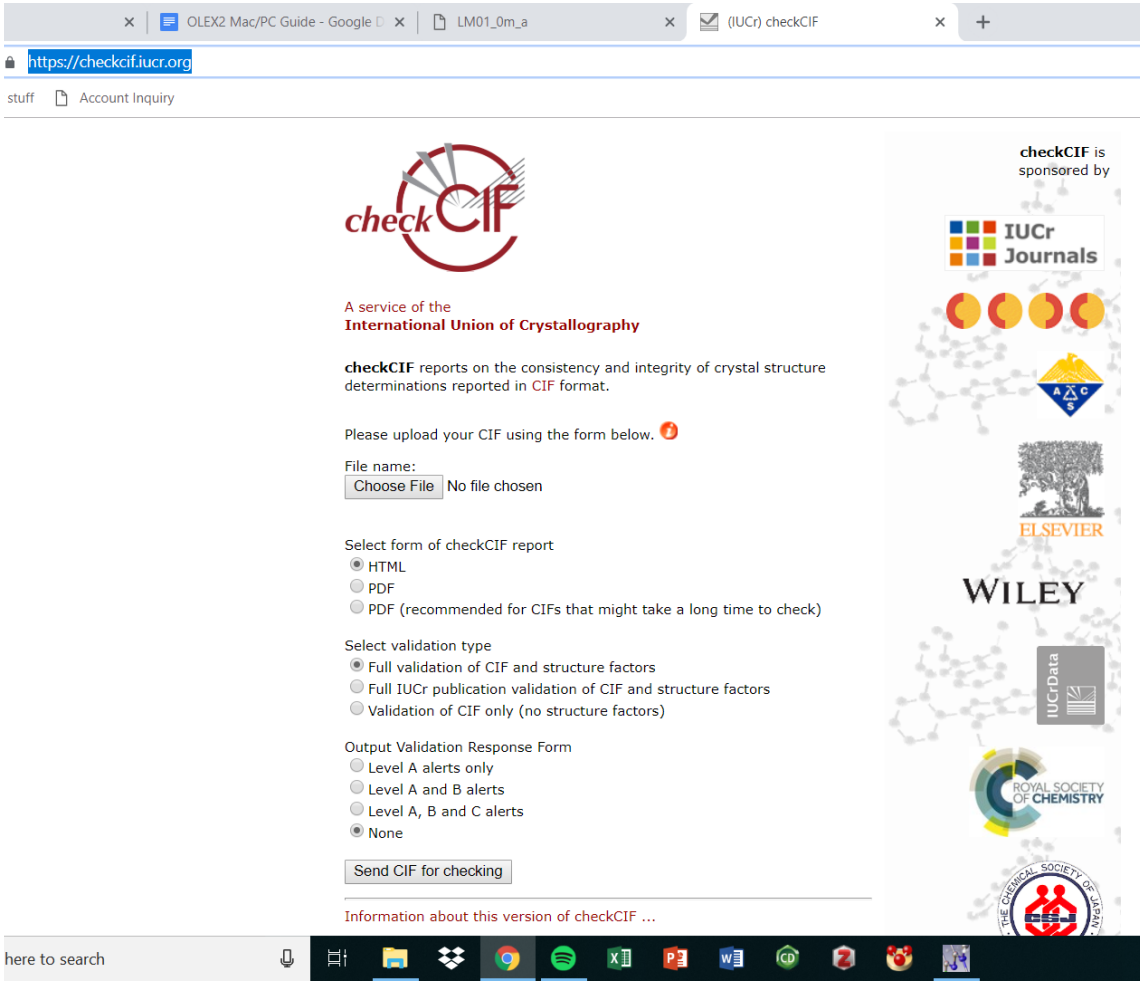
21. Now we need to generate a crystallographic information file (CIF) and see if there are any issues with the CIF. Check the folder where you have all of the files stored for a .cif file, if there is not one generate the CIF by selecting the Report tab, this will cause a computation for a moment then a window will pop up, select ok. You will then get another pop-up window that you can exit out of and then it will open a page in your web browser. Which you can close out of. If you have the .cif file (which you should have) you can skip this step.

LM01_0m_a

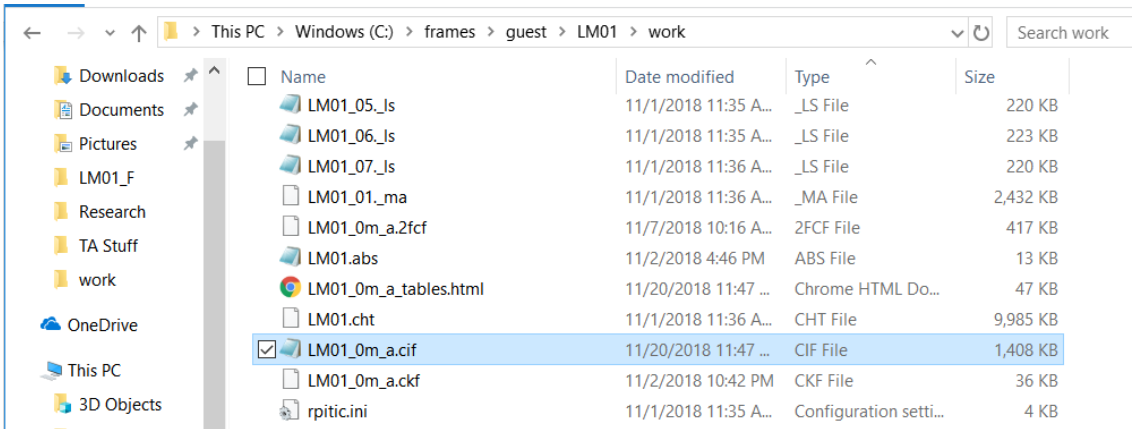
Table 1 Crystal data and structure refinement for LM01_0m_a.

Identification code	LM01_0m_a
Empirical formula	$C_{34}HN_3PS_4CoCl_{0.5}$
Formula weight	686.23
Temperature/K	113.0
Crystal system	triclinic
Space group	P-1
a/Å	9.109(13)
b/Å	13.451(11)
c/Å	14.833(12)
α/°	96.78(4)
β/°	95.10(5)
γ/°	107.45(5)
Volume/Å^3	1707(3)
Z	2
ρ_{calc}g/cm^3	1.335
μ/mm^{-1}	0.860
F(000)	679.0
Crystal size/mm^3	0.571 × 0.317 × 0.138
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.92 to 54.326
Index ranges	$-11 \leq h \leq 11$, $-17 \leq k \leq 17$, $-18 \leq l \leq 18$
Reflections collected	46926
Independent reflections	7494 [R_{int} = 0.0445, R_{sigma} = 0.0306]
Data/restraints/parameters	7494/0/406
Goodness-of-fit on F^2	1.154
Final R indexes [I>=2σ (I)]	R_1 = 0.0460, wR_2 = 0.1427
Final R indexes [all data]	R_1 = 0.0530, wR_2 = 0.1590
Largest diff. peak/hole / e Å^{-3}	1.05/-0.56

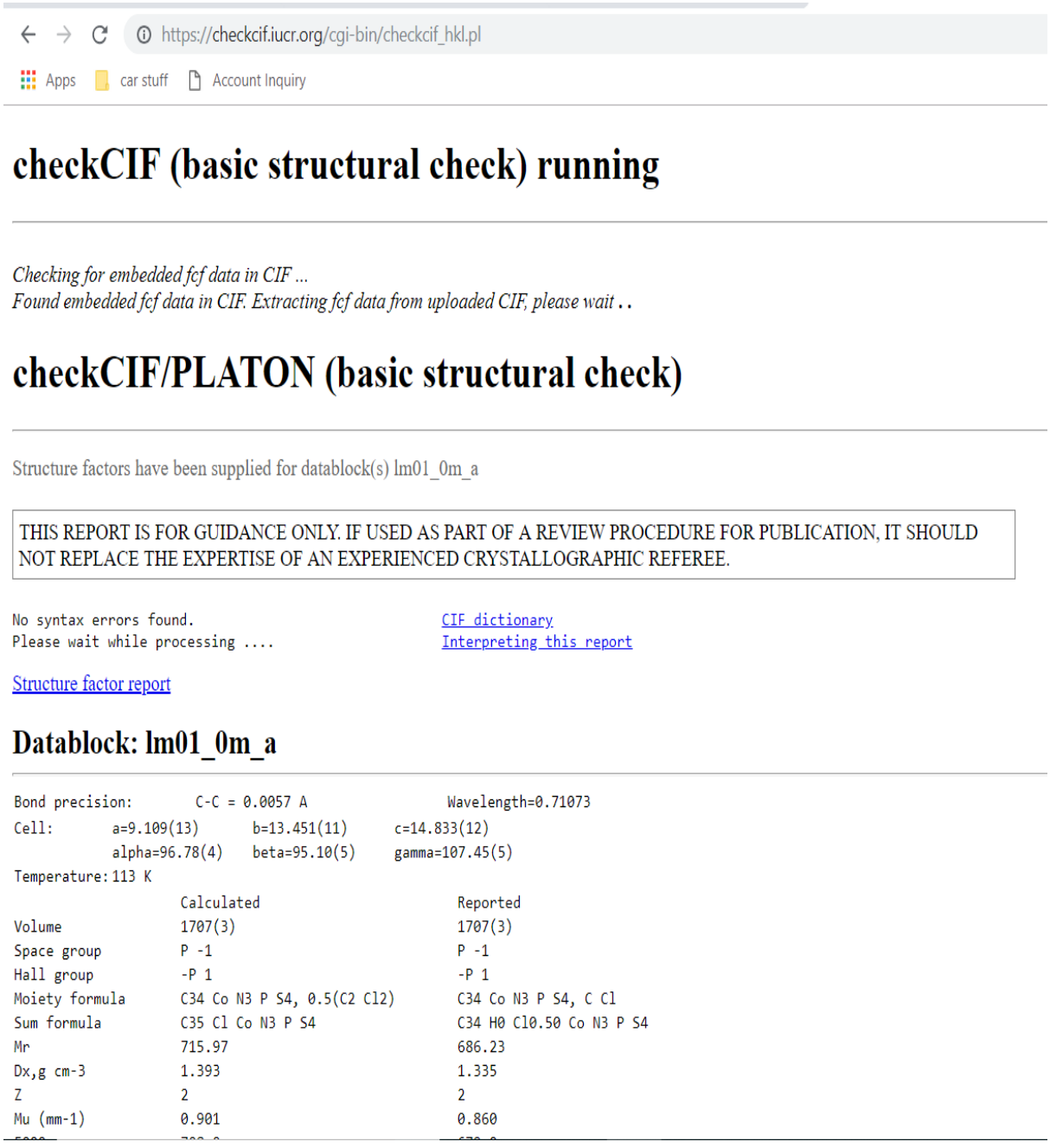
22. After making the CIF file you will need to go to" https://checkcif.iucr.org" to check the suitability of the CIF for publication, which will look like the following.



23. Now select your CIF file in your work folder, make sure that it is the CIF file type as well



24. Then select send CIF for checking at the bottom of the page, it may take a minute to perform, then you will be redirected to another page.



https://checkcif.iucr.org/cgi-bin/checkcif_hkl.pl

Apps car stuff Account Inquiry

checkCIF (basic structural check) running

Checking for embedded fcf data in CIF ...
Found embedded fcf data in CIF. Extracting fcf data from uploaded CIF, please wait . .

checkCIF/PLATON (basic structural check)

Structure factors have been supplied for datablock(s) lm01_0m_a

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary
Please wait while processing .... Interpreting this report

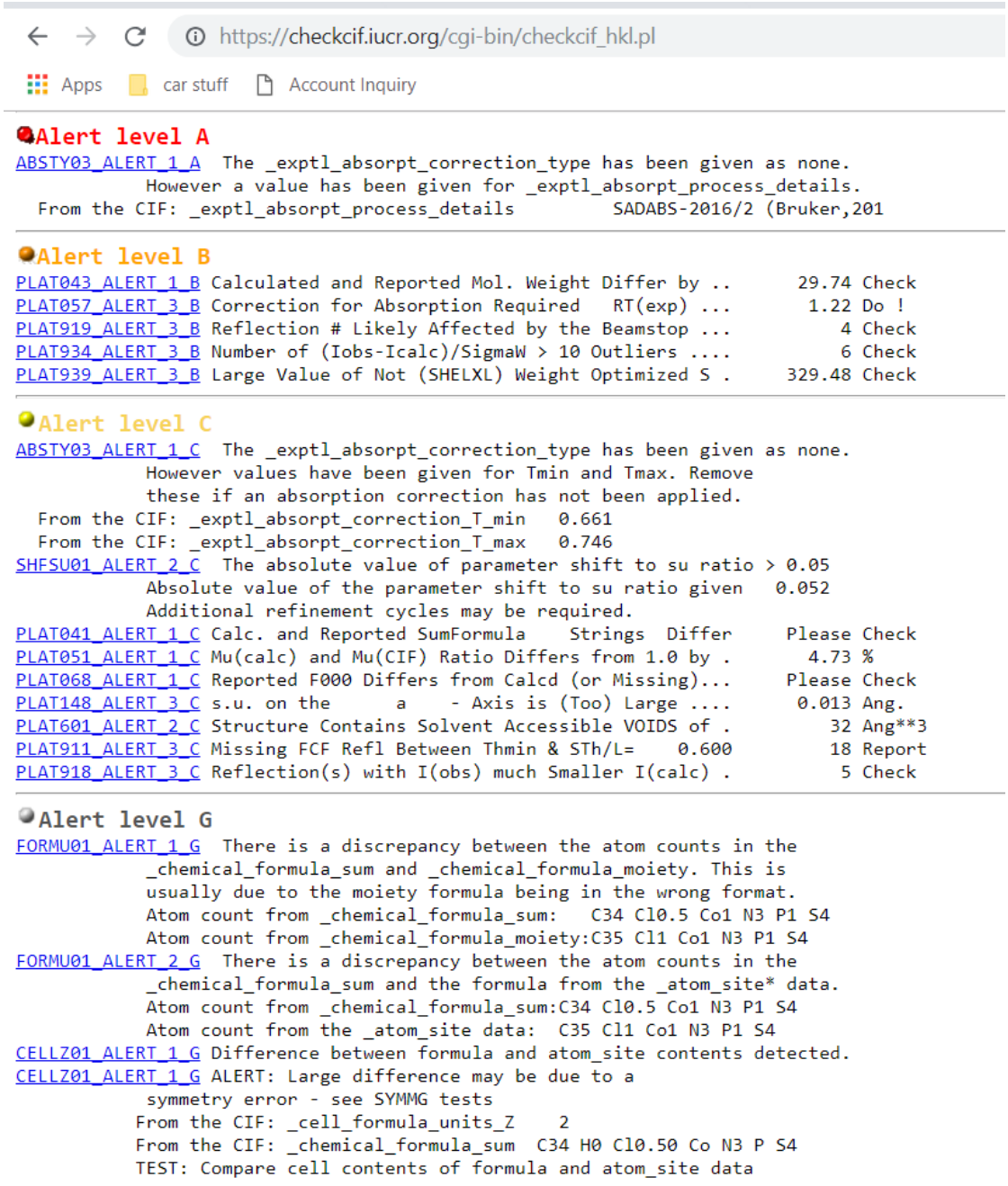
Structure factor report

Datablock: lm01_0m_a

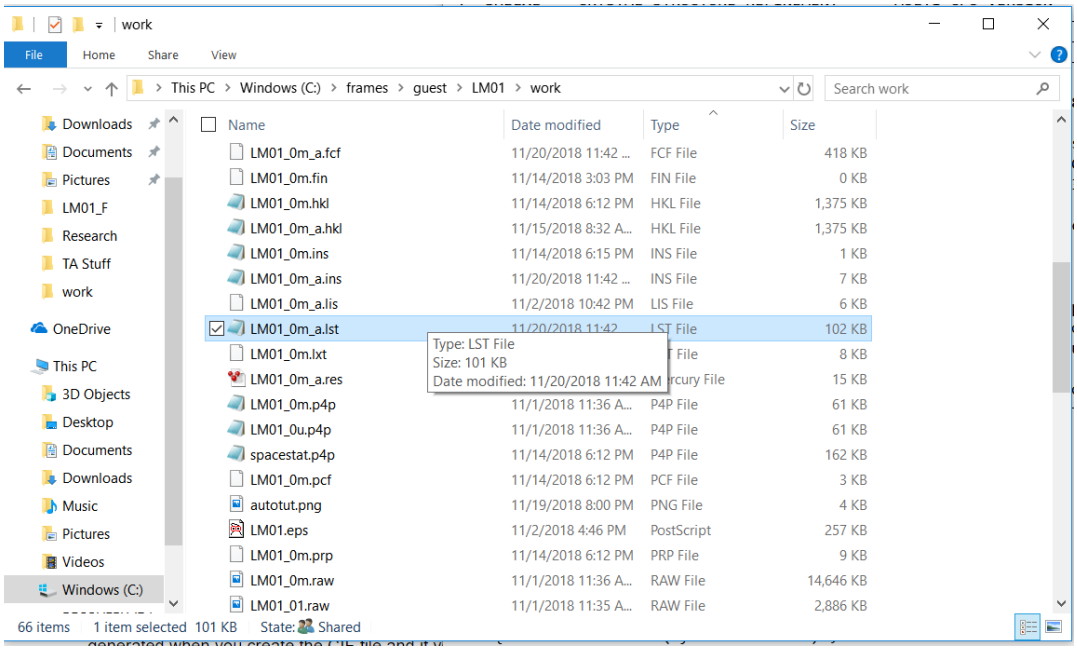
Bond precision: C-C = 0.0057 A Wavelength=0.71073
Cell: a=9.109(13) b=13.451(11) c=14.833(12)
alpha=96.78(4) beta=95.10(5) gamma=107.45(5)
Temperature: 113 K

	Calculated	Reported
Volume	1707(3)	1707(3)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C34 Co N3 P S4, 0.5(C2 Cl2)	C34 Co N3 P S4, C Cl
Sum formula	C35 Cl Co N3 P S4	C34 H0 Cl0.50 Co N3 P S4
Mr	715.97	686.23
Dx,g cm-3	1.393	1.335
Z	2	2
Mu (mm-1)	0.901	0.860

25. Scroll down until you can see the A, B, C, and G alerts. (your alerts may look different)

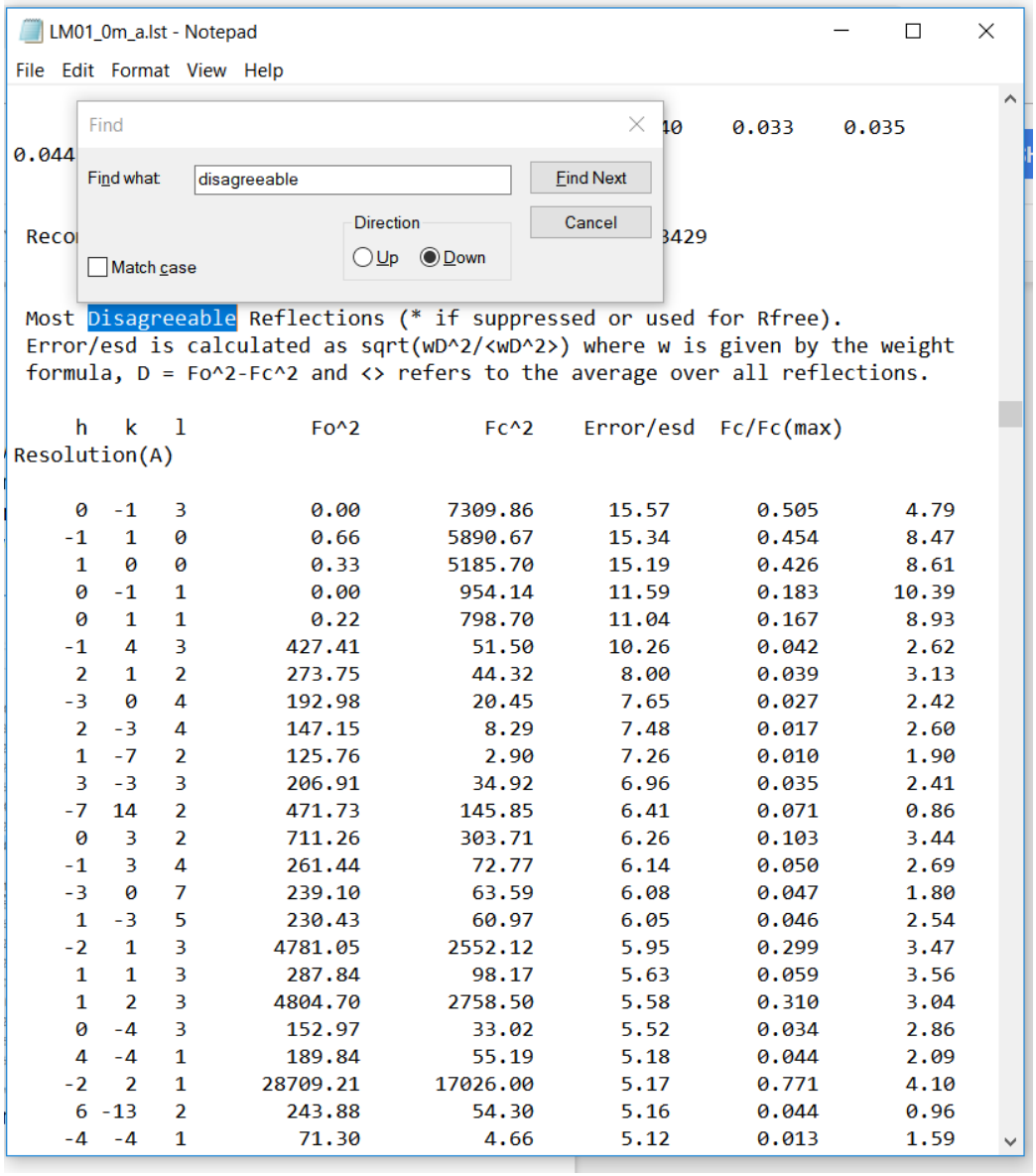


26. In order to complete the CIF file for publication, we will need to remove as many of the A, B, and C alerts as possible since these signify critical errors in the CIF.
    a. The majority of reflections can be omitted by going to the info tab, selecting the bad reflection box, and selecting omit. It can also be done as presented in the following steps.

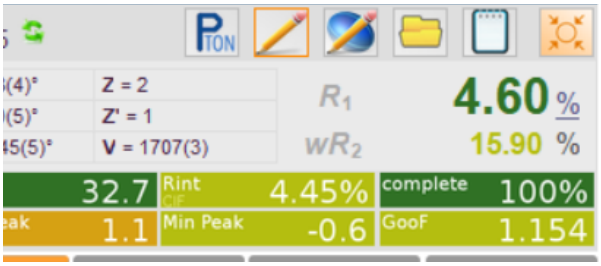


27. In programs outside of Olex editing the RES file as shown in the following steps is the best way to do this, and there are extra reflections that will need to be omitted as seen in step 33 and will need to use the following steps to alter. Let's start by removing the bad reflections due to the beam stop. To do this we will need to look in our "LST" file. Open the LST file. Once open do a find function using "control F" or "Command F" for mac,

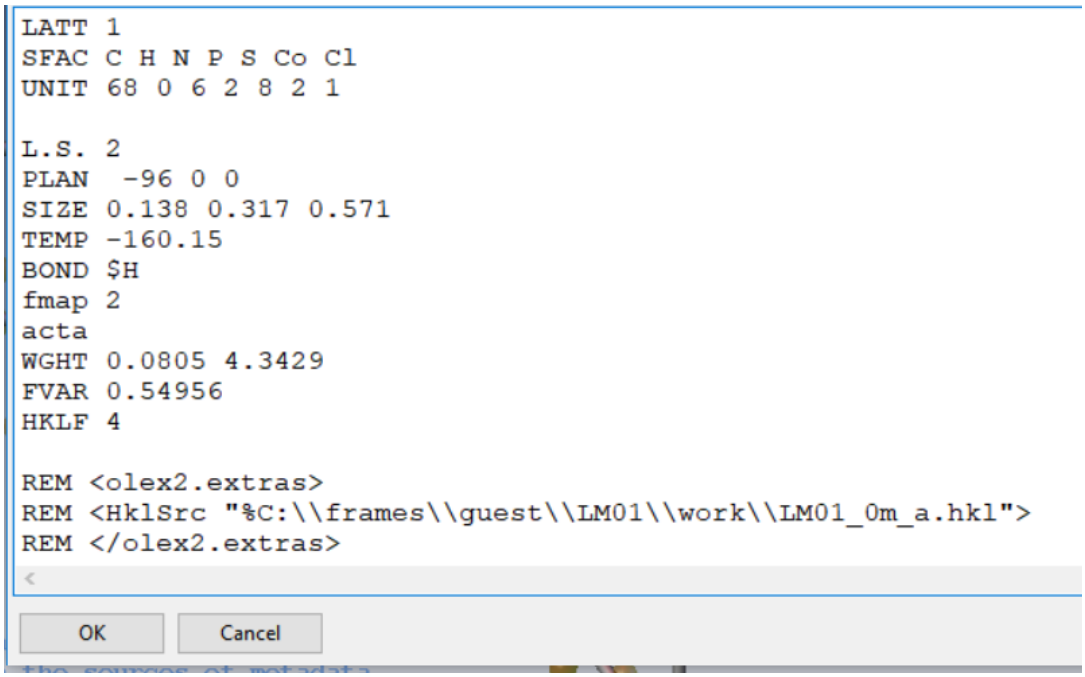
and search for the word “disagreeable.”



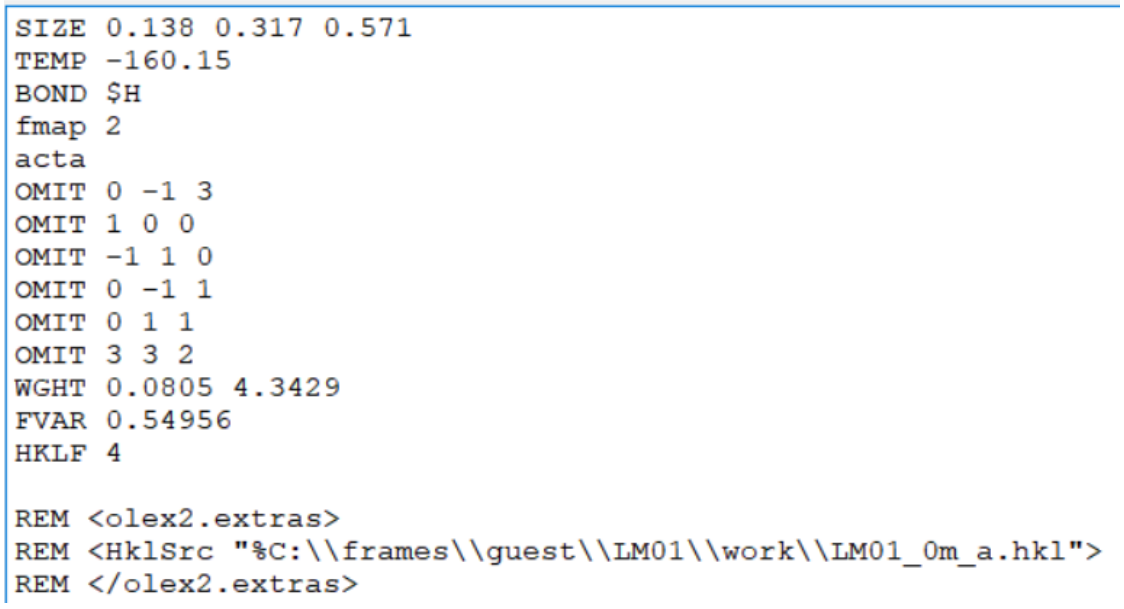
28. We will need find areas where the Fo^2 is between 1 and 0, while the Fc^2 is a much higher number. There should only be 6. Write down the HKL numbers, which are the 3 numbers in front of the Fo^2, on a separate sheet of paper.
29. Now go back into Olex^2 and select the icon with just a pencil, highlighted below.



30. After selecting this you will be able to edit your RES file, scroll down to the bottom and locate the word “acta”

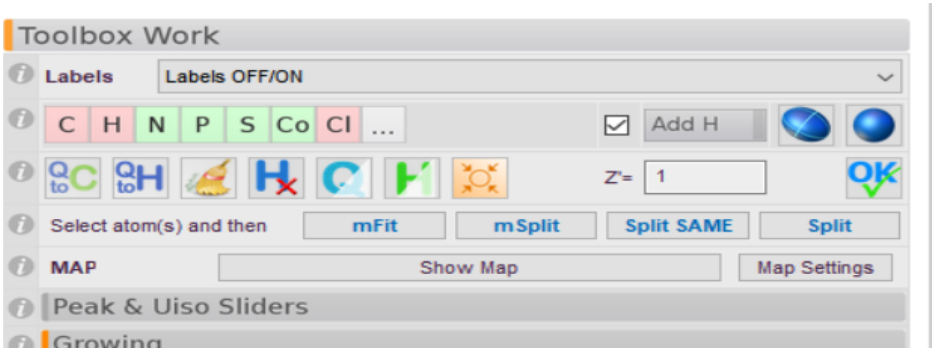


31. Hit enter after acta to go down a row and write “OMIT” then follow it with 1 set of the HKL numbers from the bad reflections. Repeat that until all the reflections have been selected to be omitted. (which can be seen in the next image/step)

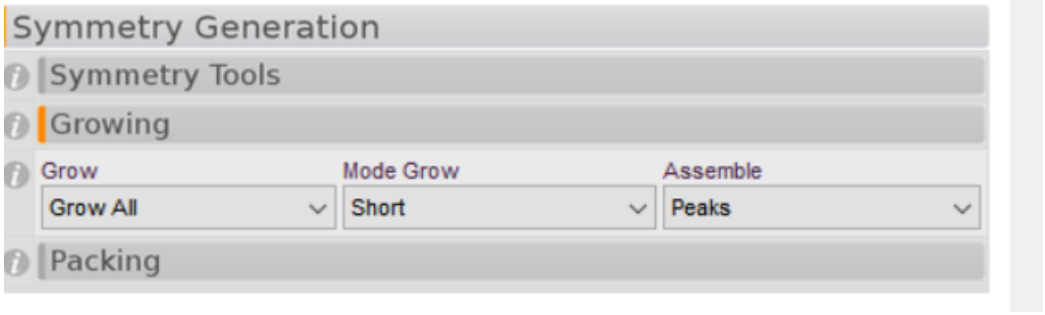


32. After doing this there are 2 other HKL reflections that are more difficult to identify than the five that were initially found, this takes a much more extensive search and because of the time that this can take to find it will be given to you just to move the tutorial along, the two extra sets are “-7 14 2,” “-2 2 1,” so additionally omit these HKL numbers as well. Select “OK” to close this window
33. After doing this refine the structure.

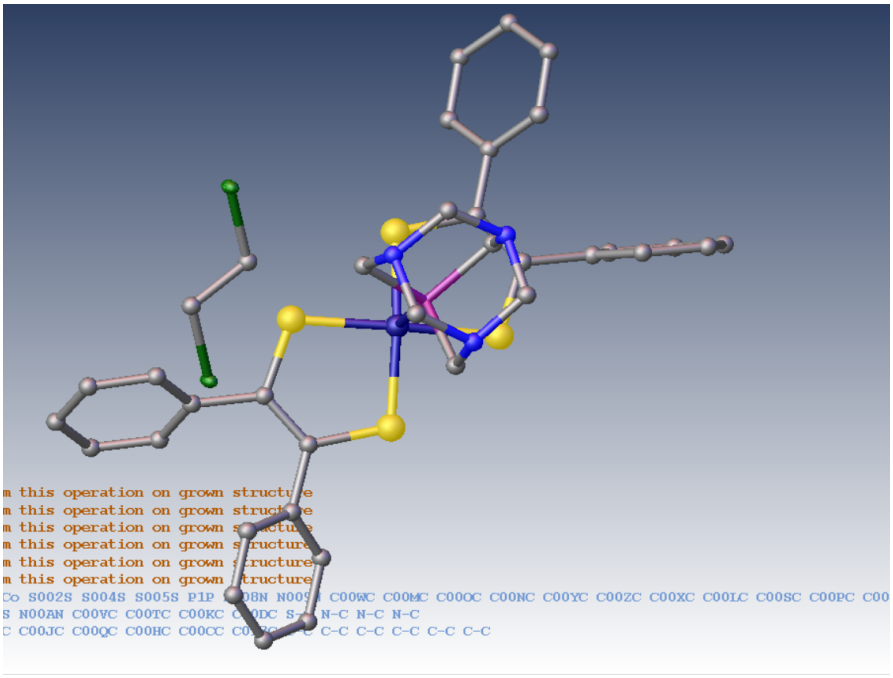
34. Now we need to add the hydrogen atoms to the system by going to the work tab and then the “toolbox work” insert and selecting add H in the box shown below.



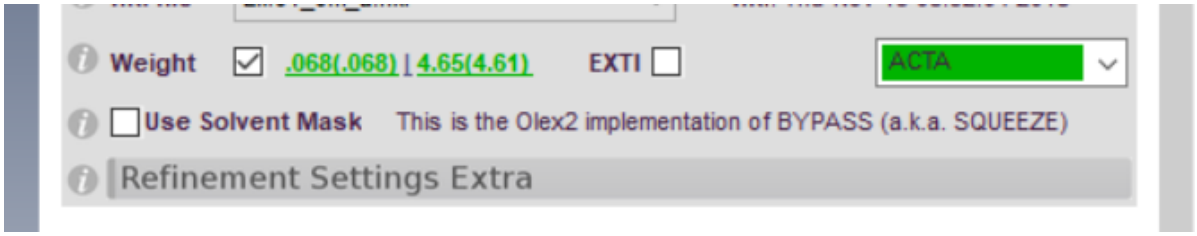
35. Now we need to take the mirrored solvent which is dichloroethane, and make it so that it is a whole molecule. To do this we need to “GROW it, go to the View tab then select the Symmetry Generation insert and in the three windows under the growing field have the three fields as indicated in the following image. You will need to select the grow all option even if it is pre-selected when you open the growing menu.



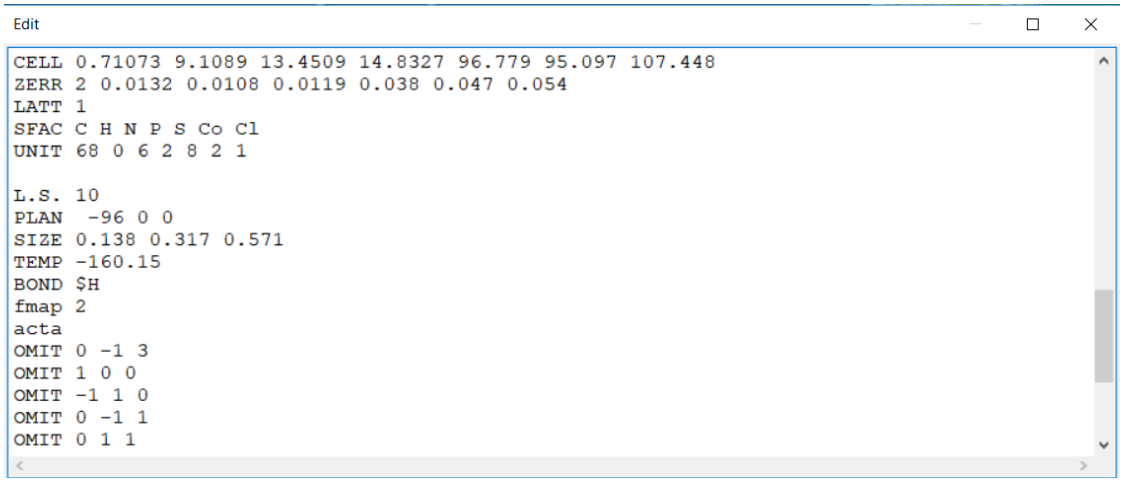
36. This should make your dichloroethane fully visible, and it might generate another molecule that you will need to delete by selecting the atoms and pressing the delete key. (Hydrogens omitted for clarity)



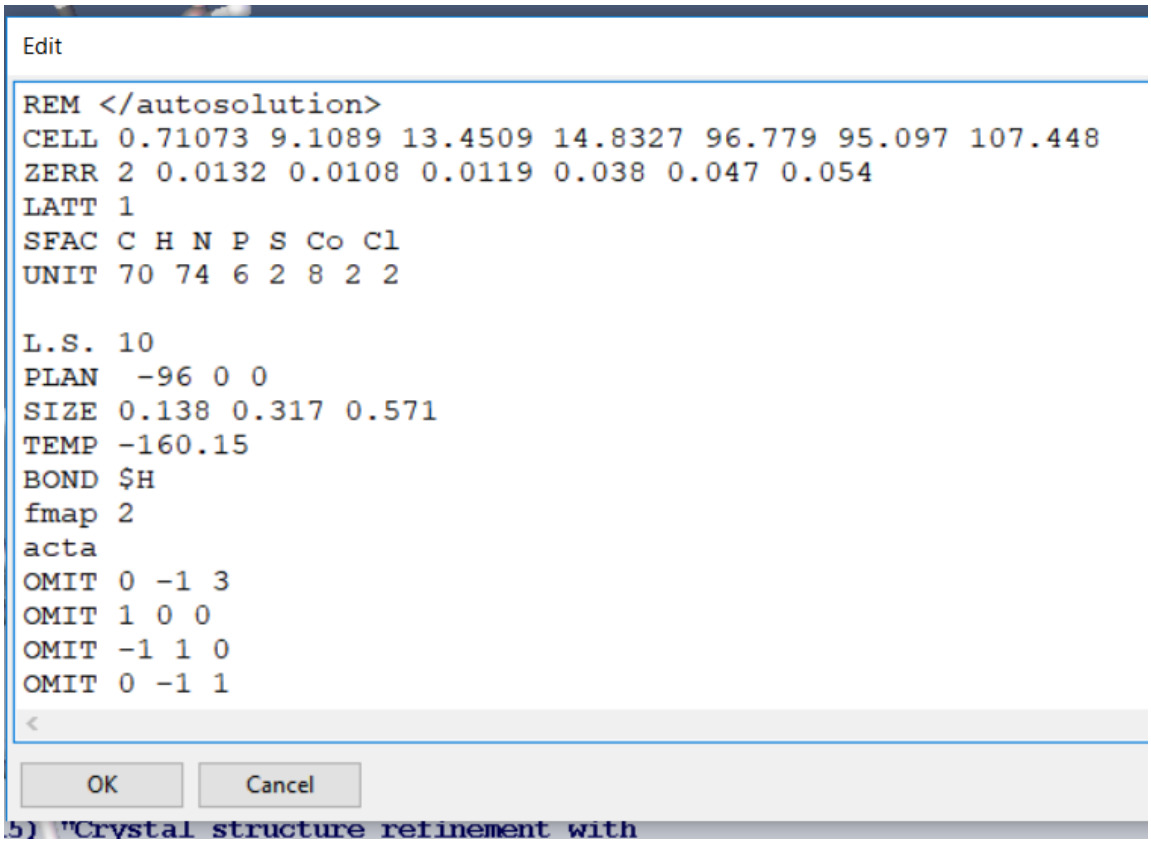
37. After making your dichloroethane we need to refine the system until the weight converges, make sure you are refining the system 10 cycles each time to make this process faster.



38. Now we will check the B alert about “Molar weight differ” by going into the RES folder like we did for omitting the reflections.

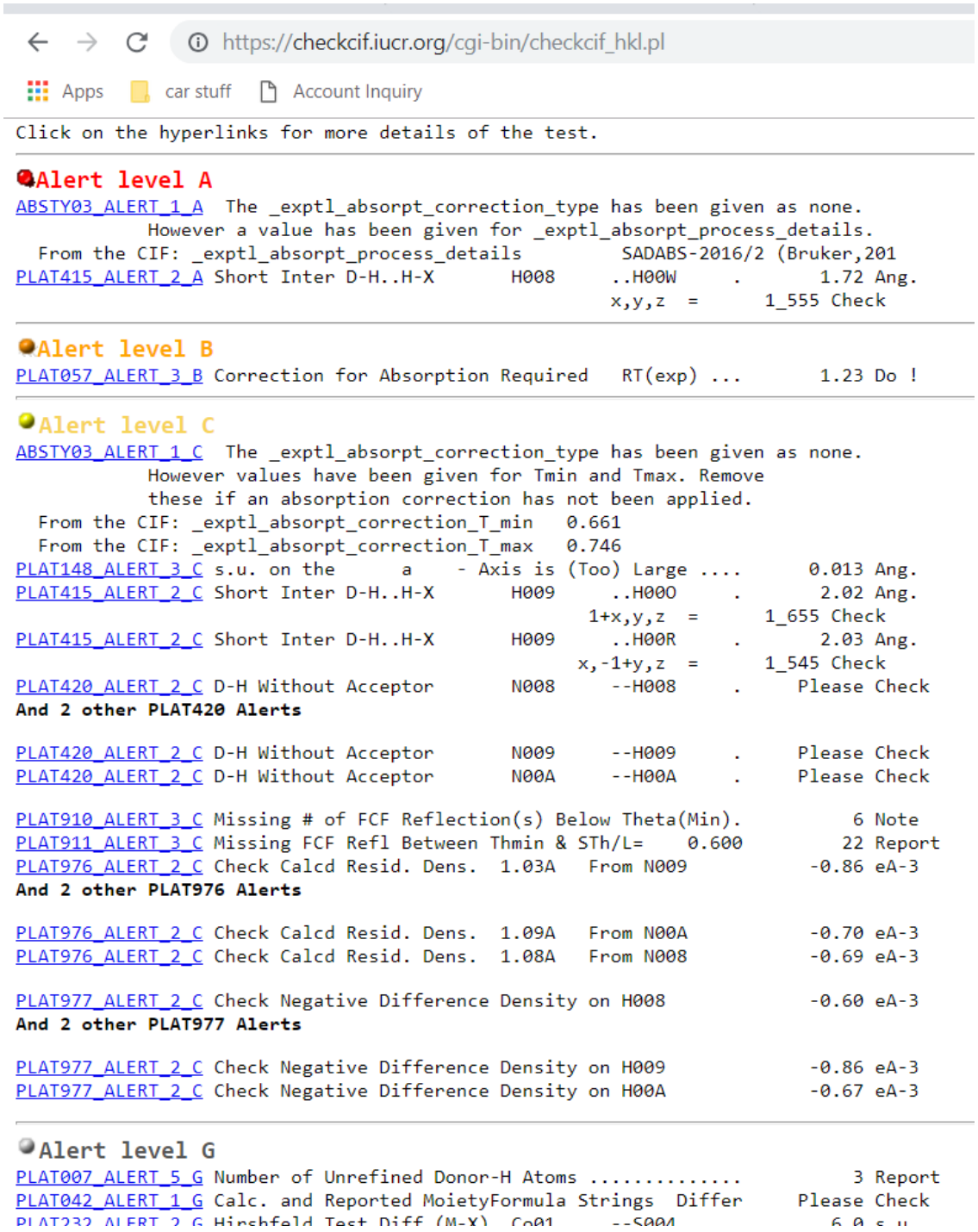


39. Notice where it says “UNIT” all of the hydrogen atoms are missing. This is an easy correction we just need to make sure that the unit reads the same as the Molecular formula (C35 H37 Co1 S4 N3 P1 Cl1) that we should have, but due to there being two of these molecules in one unit cell we will need to double all of these values. Which should look like the following picture.



40. Once the formula moieties match up, we will run another check CIF through IUCr

41. After running the check CIF, you should get the following errors (or similar)



https://checkcif.iucr.org/cgi-bin/checkcif_hkl.pl

Apps car stuff Account Inquiry

Click on the hyperlinks for more details of the test.

Alert level A

ABSTY03_ALERT_1_A The _exptl_absorpt_correction_type has been given as none.
However a value has been given for _exptl_absorpt_process_details.
From the CIF: _exptl_absorpt_process_details SADABS-2016/2 (Bruker,201
PLAT415_ALERT_2_A Short Inter D-H..H-X H008 ..H00W . 1.72 Ang.
x,y,z = 1_555 Check

Alert level B

PLAT057_ALERT_3_B Correction for Absorption Required RT(exp) ... 1.23 Do !

Alert level C

ABSTY03_ALERT_1_C The _exptl_absorpt_correction_type has been given as none.
However values have been given for Tmin and Tmax. Remove
these if an absorption correction has not been applied.
From the CIF: _exptl_absorpt_correction_T_min 0.661
From the CIF: _exptl_absorpt_correction_T_max 0.746
PLAT148_ALERT_3_C s.u. on the a - Axis is (Too) Large .... 0.013 Ang.
PLAT415_ALERT_2_C Short Inter D-H..H-X H009 ..H00O . 2.02 Ang.
1+x,y,z = 1_655 Check
PLAT415_ALERT_2_C Short Inter D-H..H-X H009 ..H00R . 2.03 Ang.
x,-1+y,z = 1_545 Check
PLAT420_ALERT_2_C D-H Without Acceptor N008 --H008 . Please Check
And 2 other PLAT420 Alerts

PLAT420_ALERT_2_C D-H Without Acceptor N009 --H009 . Please Check
PLAT420_ALERT_2_C D-H Without Acceptor N00A --H00A . Please Check

PLAT910_ALERT_3_C Missing # of FCF Reflection(s) Below Theta(Min). 6 Note
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L= 0.600 22 Report
PLAT976_ALERT_2_C Check Calcd Resid. Dens. 1.03A From N009 -0.86 eA-3
And 2 other PLAT976 Alerts

PLAT976_ALERT_2_C Check Calcd Resid. Dens. 1.09A From N00A -0.70 eA-3
PLAT976_ALERT_2_C Check Calcd Resid. Dens. 1.08A From N008 -0.69 eA-3

PLAT977_ALERT_2_C Check Negative Difference Density on H008 -0.60 eA-3
And 2 other PLAT977 Alerts

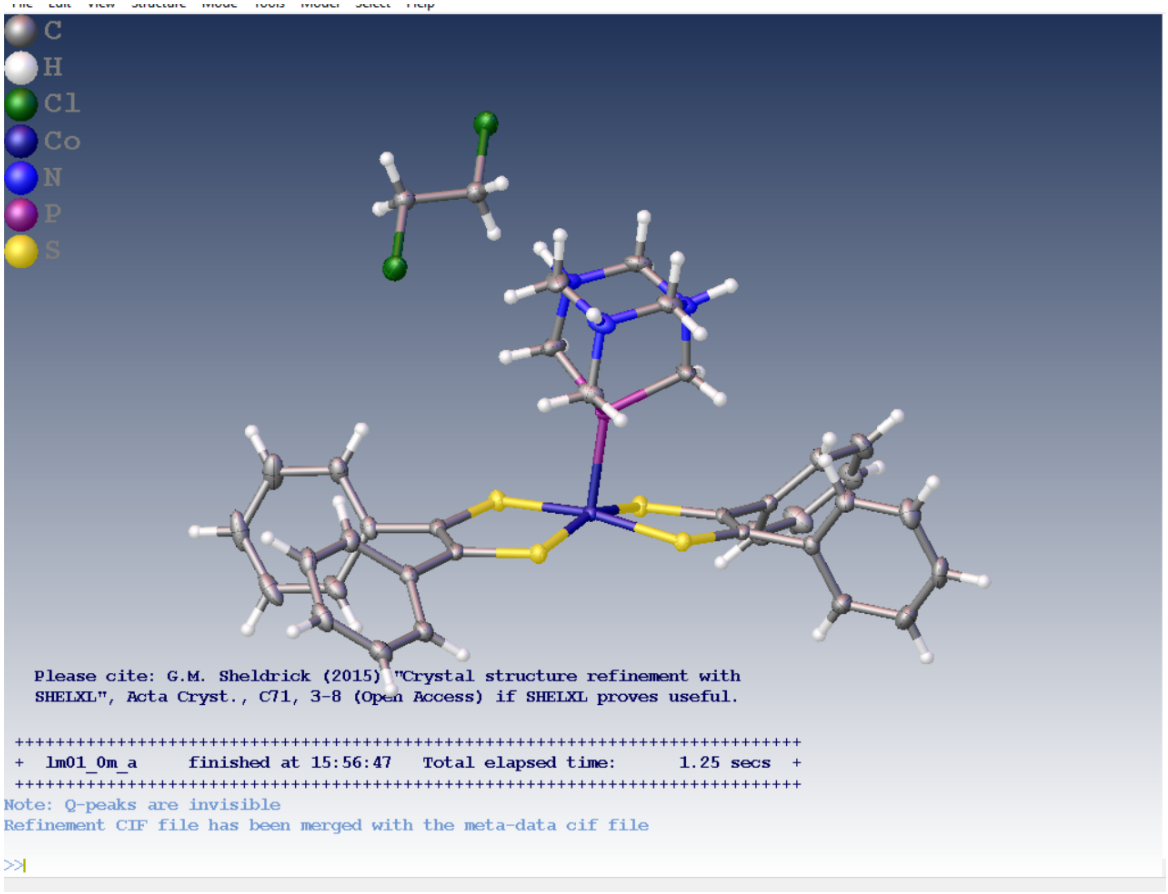
PLAT977_ALERT_2_C Check Negative Difference Density on H009 -0.86 eA-3
PLAT977_ALERT_2_C Check Negative Difference Density on H00A -0.67 eA-3

Alert level G

PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..... 3 Report
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings Differ Please Check
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Co01 --S004 6.0 s.u.

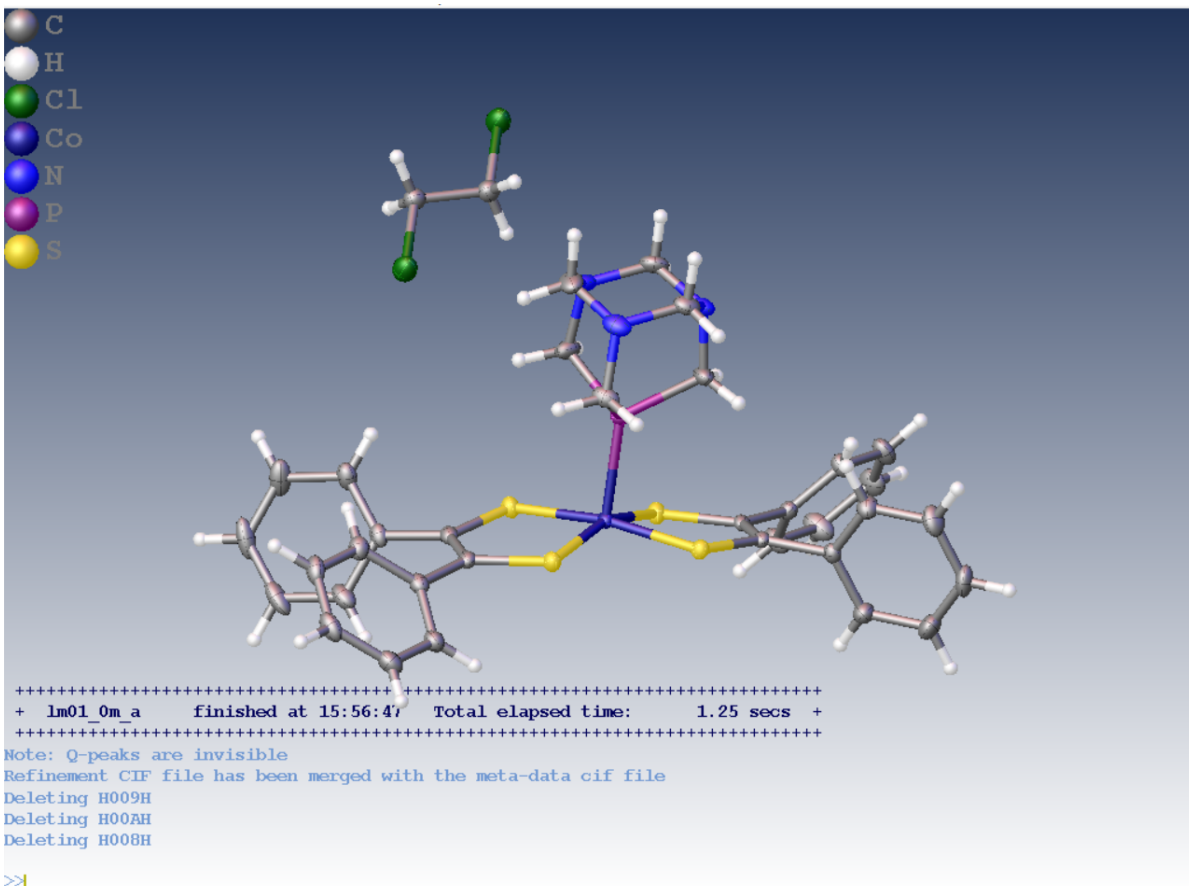
42. Notice how there are a lot of C alerts now we can address those by looking at the hydrogen atoms that are present in the system to make sure that all of them should be there.

43. Looking at the complex with the hydrogens attached we should see the following picture.

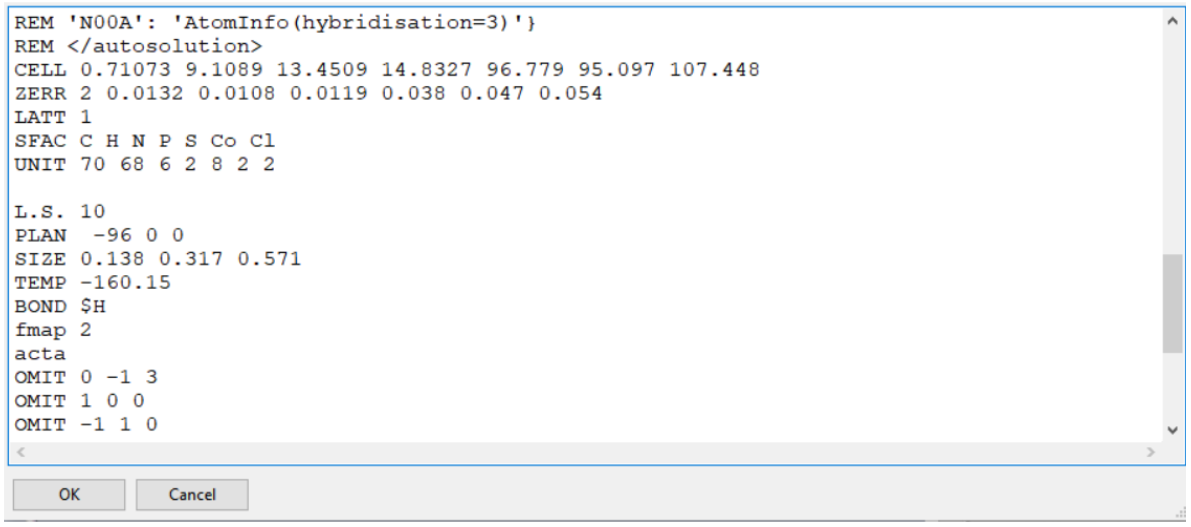


44. Make sure that all of the hydrogens in the nitrogen cage-like structure are supposed to be there, everything in this complex is neutrally charged in the adamantane “cage”

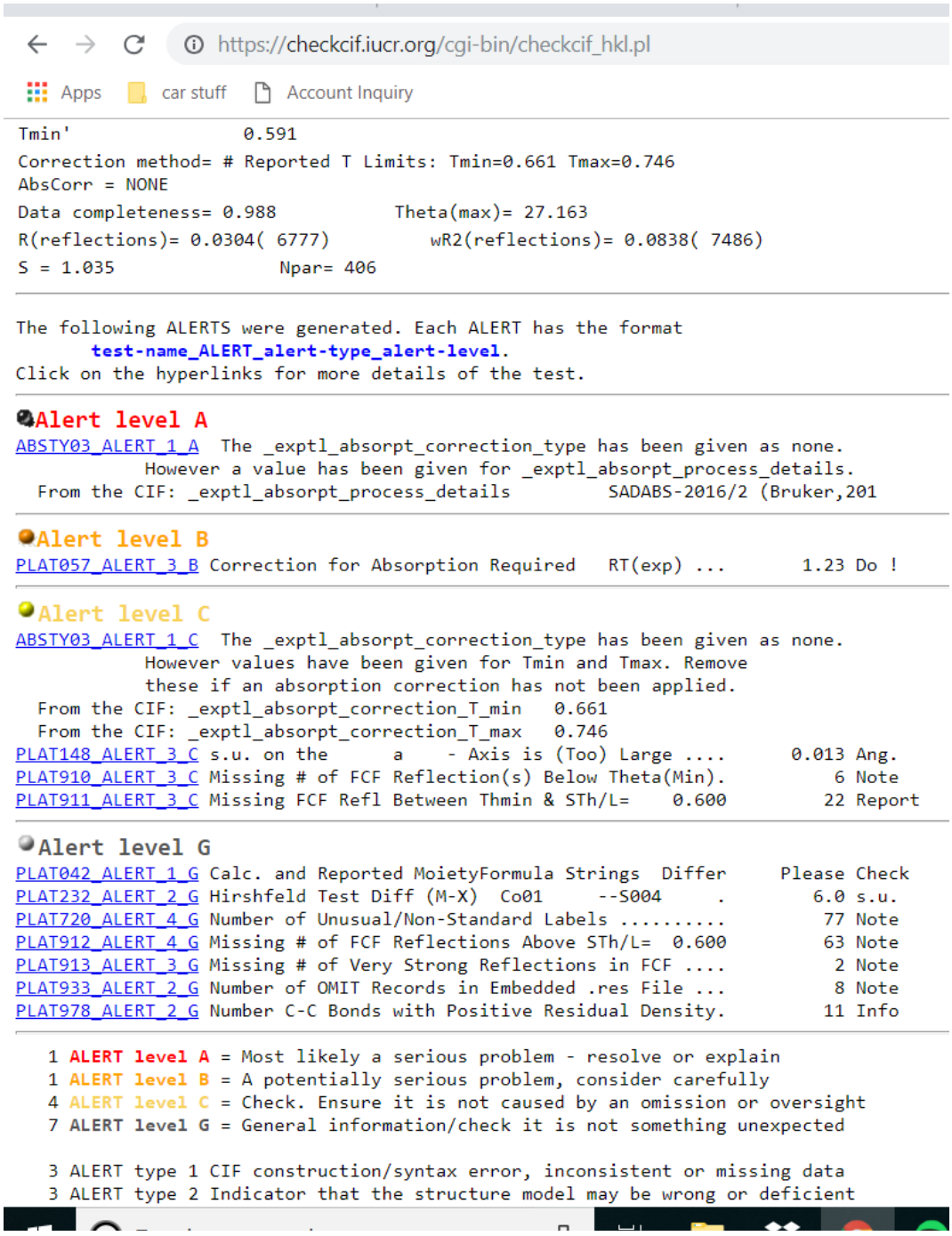
45. You should notice that there are 3 extra hydrogen atoms that will need to be deleted, after doing so your molecule should look like the following.



46. Now that we have removed those hydrogen atoms from the structure, we will need to remove them from the formula moiety as well, remember that we have to count for 2 of these complexes in every unit cell.



47. Once these hydrogen atoms are taken care of, we can run another refinement then another check CIF through IUCr. You should get the following.



48. To fix the remaining A issues (If there are any of the following type) open the CIF, and Search for “_cell_formula_unit_z” and under it put the following table in by typing each component into the correct column. These are experimental parameters collected during the measurement.
    a. If there are many A, B, and C alerts (>5), this could be due to updates made after this tutorial. However, the purpose of this tutorial is to familiarize you with the software and not how to fix complex issues. You may skip these alerts and finish the tutorial using the Finalized_CIF.cif file.

_cell_measurement_refln_used	28282
_cell_measurement_temperature	113(2)
_cell_measurement_theta_min	4.577
_cell_measurement_theta_max	54.196

next search for “_exptl_crystal_density_meas” directly above this type in “_exptl_crystal_description” and “_exptl_crystal_color” then on the right column state ‘prism’ and ‘black’ respectively. The apostrophes are necessary.
under “_exptl_crystal_F_000” put in the following table by typing out each component in the appropriate column.

_exptl_crystal_size_max	0.571
_exptl_crystal_size_mid	0.317
_exptl_crystal_size_min	0.138
_exptl_absorpt_correction_type	‘multi-scan’
_exptl_absorpt_correction_T_min	0.6611
_exptl_absorpt_correction_T_max	0.7455
_exptl_absorpt_process_details	'SADABS-2016/2 (Krause et al. 2015)'

Then find “_differn_reflns_number” and above that insert
“_diffrn_measurement_device_type” answered with 'Bruker D* Venture Kappa'

49. Now validate the last C alerts by writing a validation report into your CIF file. To do this go back to the main check CIF page and make the same selections as in the following image.

50. Run the CIF and go to the segment below the alerts and copy the validation report form.

```
Alert level C
PLAT910_ALERT_3_C Missing # of FCF Reflection(s) Below Theta(Min).          6 Note
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600         21 Report

Alert level G
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings  Differ      Please Check
PLAT154_ALERT_1_G The s.u.'s on the Cell Angles are Equal ..(Note)       0.003 Degree
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Co01     --S004     .        6.0 s.u.
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels .........          79 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600         5 Note
PLAT913_ALERT_3_G Missing # of Very Strong Reflections in FCF ....         2 Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ...         7 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.        11 Info

   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   2 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   8 ALERT level G = General information/check it is not something unexpected

   2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   3 ALERT type 2 Indicator that the structure model may be wrong or deficient
   3 ALERT type 3 Indicator that the structure quality may be low
   2 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

Validation response form

Please find below a validation response form (VRF) that can be filled in and pasted into your CIF.

```
# start Validation Reply Form
_vrf_PLAT910_lm01_0m
;
PROBLEM: Missing # of FCF Reflection(s) Below Theta(Min).          6 Note
RESPONSE: ...
;
_vrf_PLAT911_lm01_0m
;
PROBLEM: Missing FCF Refl Between Thmin & STh/L=    0.600         21 Report
RESPONSE: ...
;
# end Validation Reply Form
```

51. Make sure that all the red text is highlighted and paste it into the CIF file at the very top below “data_lm01_0m”. Make sure there is a blank line before and after the validation form is inserted.

```
data_lm01_0m

# start Validation Reply Form
_vrf_PLAT910_lm01_0m
;
PROBLEM: Missing # of FCF Reflection(s) Below Theta(Min).          6 Note
RESPONSE: ...
;
_vrf_PLAT911_lm01_0m
;
PROBLEM: Missing FCF Refl Between Thmin & STh/L=    0.600         21 Report
RESPONSE: ...
;
# end Validation Reply Form

_audit_creation_date               2018-11-17
_audit_creation_method
;
Olex2 1.2
(compiled May 18 2018 14:05:52 for OlexSys, GUI svn.r5506)
;
_shelx_SHELXL_version_number       '2018/3'
_audit_contact_author_address      ?
_audit_contact_author_email        ?
_audit_contact_author_name         ''
_audit_contact_author_phone        ?
_publ_contact_author_id_orcid      ?
_publ_section_references
;
Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H.
 (2009), J. Appl. Cryst. 42, 339-341.
```

52. The response for the missing number of reflections is due to “Omitted reflections from the beam stop.”
53. The response for the missing FCF reflections between Thmin and STh/L is due to “Reflections replaced by fast scans due to overload.”

54. Put the proper quotation in the proper response location and save the CIF.

```
data_lm01_0m

# start Validation Reply Form
_vrf_PLAT910_lm01_0m
;
PROBLEM: Missing # of FCF Reflection(s) Below Theta(Min).          6 Note
RESPONSE: Omitted reflections from beamstop.
;
_vrf_PLAT911_lm01_0m
;
PROBLEM: Missing FCF Refl Between Thmin & STh/L=    0.600         21 Report
RESPONSE: Reflections replaced by fast scans due to overload.
;
# end Validation Reply Form

_audit_creation_date               2018-11-17
_audit_creation_method
;
Olex2 1.2
(compiled May 18 2018 14:05:52 for OlexSys, GUI svn.r5506)
;
_shelx_SHELXL_version_number       '2018/3'
_audit_contact_author_address      ?
_audit_contact_author_email        ?
_audit_contact_author_name         ''
_audit_contact_author_phone        ?
_publ_contact_author_id_orcid      ?
_publ_section_references
;
Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H.
 (2009), J. Appl. Cryst. 42, 339-341.

Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.

Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.
```

55. Run the CIF through IUCr and it should look like the following complete CIF.

```
The following ALERTS were generated. Each ALERT has the format
      test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.
```

Alert level C

PLAT910_ALERT_3_C Missing # of FCF Reflection(s) Below Theta(Min). 6 Note

Author Response: Omitted reflections from beamstop.

PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L= 0.600 21 Report

Author Response: Reflections replaced by fast scans due to overload.

Alert level G

```
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings  Differ     Please Check
PLAT154_ALERT_1_G The s.u.'s on the Cell Angles are Equal ..(Note)      0.003 Degree
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  Co01     --S004     .       6.0 s.u.
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels .........        79 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600       5 Note
PLAT913_ALERT_3_G Missing # of Very Strong Reflections in FCF ....       2 Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ...       7 Note
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```

```
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```