Hands-on sessions: structure solution and refinement for small-molecules

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You will have the opportunity to work on five small-molecule structures for which data will be supplied via download. The structures will each have different challenges and increasing difficulty. The aim is first to get you used to using Olex², structure solution software (mainly SHELXT) and SHELXL for refinement, so that you can take a straightforward structure through to completion, including CIF completion and validation. The remaining structures are designed to expose you to some common situations, such as the molecule not being that predicted by the chemist, more or less than one molecule in the asymmetric unit (Z' ≠ 1), working out what an additional unknown species is in the structure (e.g. unexpected solvent), and dealing with simple and very complex disorder.

All of the example structures are real cases. While all examples involve discrete organic or organometallic molecules, one example will show you what you see in the asymmetric unit when modelling a polymeric structure, such as a MOF.

The following pages give you some initial information about each example structure and a brief list of the main tasks you have to complete. During the sessions, we will guide you through the various steps, but you should try to complete each structure fully yourself.

In the downloaded folder for each structure, you will find the starting SHELX .ins (instructions) and .hkl (unmerged reflections) files and the information sheet for the specific example. When you have finished each structure, you can compare your results (.cif and .res files) with my results, which are derived in the way that I normally use, although alternative strategies might be possible and each tutor might have slightly different suggestions. My results and some notes on each structure, which were issued to the tutors, are in the "answer" folder for each structure. However, we recommend that you try each structure as best you can for yourself first, following the guidance we will give in the sessions, before looking at the answer. You will gain more experience that way. If you are stuck, please do not hesitate to ask one of the tutors or me.

Example structure 1 (ex1)

The reflection data file ex1.hkl and a starting ex1.ins without space group information are supplied along with ex1.cif_od, which is a partial CIF containing information about the data collection experiment. Start Olex² according to the handbook. The data below can be used when required.

Crystallised from	CH_2Cl_2
Empirical formula	$C_{14}H_{11}N_3Se$
Crystal colour, habit	pale-orange, prism
Crystal dimensions [mm]	0.19 0.22 0.45
Temperature [K]	160
Wavelength	Mo Kα: 0.71073 Å

Rigaku Oxford Diffraction XtaLAB Synergy Diffractometer
10504 reflections with 3.6° < θ < 32.3° were used for unit cell refinement
Crystal system, Bravais lattice: monoclinic primitive

a (Å)	11.2228(3)
b (Å)	15.8677(5)
c (Å)	7.4868(2)
α (°)	90.0
β (°)	94.569(3)
γ (°)	90.0
Volume (A³)	1329.02(7)

Multi-scan absorption correction applied

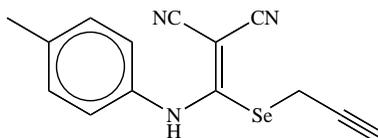|	
Absorption correction factors (min; max)	0.713; 1.000
Final Data Set	
Total number of integrated reflections	20268
Total number of unique reflections	4301
Data completeness	100.0%
Theta range	3.4°-32.6°
Overall R-merge (linear)	0.0264

Tasks:
Determine & confirm the crystal system, Bravais lattice type, space group – e.g. PLATON SPGRfromEX. What is *Z*?
Solve the structure
Check for correct element assignments
Assign a logical sequence of atom manes and numbers
Refine anisotropically
Find all H-atoms in a difference map to ensure they exist at the expected locations. They can then be optimised and constrained as riding, but refine the amine H.
Look at the methyl group. Are there disordered H here? If so, model correctly.
Refine to convergence, with optimised weights, check if extinction correction needed.
Check .lst file for information like poor weights, poor ADPs, poor Fo/Fc agreement, residual peaks. Attend to if necessary.
Does the ADP view of the molecule look OK to the eye?
Complete the CIF with all necessary information.
Validate the CIF.
What motif is formed by the classic hydrogen-bonding interactions?

Example structure 2 (ex2)

The reflection data ex2.hkl and a starting ex2.ins without space group information are supplied. A chemist has synthesised the following cation: $C_{26}H_{28}N_4O_2Zn$. The anion is a simple species, but unknown.
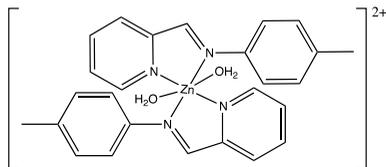
Crystallised from	MeCN
Crystal colour, habit	light yellow, prism
Crystal dimensions [mm]	$0.10 \times 0.17 \times 0.22$
Temperature [K]	160(1)
Wavelength [Å]	0.71073
Reflections for cell determination	16721
2θ range for cell determination [°]	4–65
Unit cell parameters $\quad a$ [Å]	19.7280(3)
b [Å]	9.41866(12)
c [Å]	14.5758(2)
α, β, γ [°]	90, 90, 90
V [Å^3]	2708.34(6)
Scan type	ω
$2\theta_{(max)}$ [°]	64.7
Transmission factors (min; max)	0.796; 1.000
Total reflections measured	40574
Diffractometer	Agilent SuperNova

Tasks:

Determine & confirm the crystal system, space group and *Z*.

Attempt to solve the structure. What do you find initially for the cation? Does the chemist have the expected cation, or not?

What is the anion? How can you exclude possible alternative anionic species?

What is the stoichiometry of the ions?

Complete the full refinement of the structure, as before, being sure to check the atom assignments and the information in the .lst file. The water H atoms can be refined isotropically.
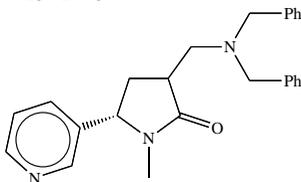
Complete the CIF with all necessary information.

Validate the CIF.

What motif is formed by the classic hydrogen-bonding interactions?

Example structure 3 (ex3)

The reflection data ex3.hkl and a starting ex3.ins without space group information are supplied. The chemist expects: $C_{25}H_{27}N_3O$

Crystallised from		EtOAc / hexane
Crystal colour, habit		colourless, prism
Crystal dimensions [mm]		$0.10 \times 0.12 \times 0.20$
Temperature [K]		160(1)
Wavelength [Å]		0.71073
Reflections for cell determination		1200
2θ range for cell determination [°]		4–50
Unit cell parameters	a [Å]	9.6997(2)
	b [Å]	9.6997(2)
	c [Å]	23.9338(4)
	α, β, γ [°]	90, 90, 120
	V [Å^3]	1950.11(7)
Scan type		ω
$2\theta_{(max)}$ [°]		50
Transmission factors (min; max)		0.926; 1.000
Total reflections measured		21947
Diffractometer		Nonius KappaCCD

Tasks:

Determine & confirm the crystal system, Bravais lattice type, space group and Z.

Attempt to solve the structure. What do you find initially? What is wrong (if anything)?

Think about the concepts you might use to get an idea of what the true structure is. Remember that the result must also make chemical sense.

Is this a chiral molecule? Is the crystal enantiomerically pure? How do you know?

How would you invert this structure?

Complete and check the structure fully, as you did for exercise 1.

Example structure 4 (ex4)

The reflection data ex4.hkl and a starting ex4.ins without space group information are supplied. A chemist has synthesised the following complex: $[Au(C_{27}H_{36}N_2)(C_6F_5)Cl_2]$.
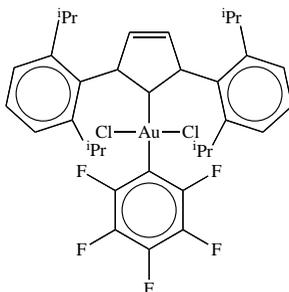
Crystallised from	hexane / CH_2Cl_2
Crystal colour, habit	colourless, prism
Crystal dimensions [mm]	$0.20 \times 0.25 \times 0.29$
Temperature [K]	160(1)
Wavelength [Å]	0.71073
Reflections for cell determination	53161
2θ range for cell determination [°]	4–61
Unit cell parameters a [Å]	21.92977(14)
b [Å]	14.42665(10)
c [Å]	23.84439(19)
α, β, γ [°]	90, 102.2246(7), 90
V [Å^3]	7372.67(9)
Scan type	ω
2θ(max) [°]	60.7
Transmission factors (min; max)	0.774; 1.000
Total reflections measured	94556
Diffractometer	Agilent SuperNova

Tasks:
Determine & confirm the crystal system, space group and Z.
Solve the structure. How many molecules of the Au-complex are present in the asymmetric unit?
What else is present? What is the stoichiometric ratio of this "other" species to the Au-complex? What is Z'?
Continue the refinement of the structure, as before, as well as possible, being sure to check the atom assignments and the information in the .lst file.
Is the "other" species disordered? Can the disorder be modelled adequately?
We will demonstrate the "last resort" alternative of the SQUEEZE procedure here to deal with the "other" species. It can be done using PLATON or with the mask feature in Olex².
After this, finalise the refinement and complete the CIF with all necessary information.
Validate the CIF.

Example structure 5 (ex5)

This is an advanced exercise on disorder and can be challenging to complete. We will discuss some of the tools available in Olex² for setting up the disorder model for refinement. It can be a bit tricky to do entirely within Olex² and some hand-editing of the .ins file sometimes helps. It is important not to try to do too many of the steps simultaneously, or the model might fly apart.The reflection data ex5.hkl and a starting ex5.ins without space group information are supplied.

$C_{23}H_{23}F_3N_2O_3S$
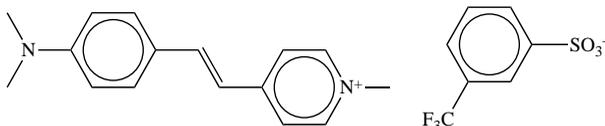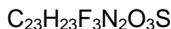
Crystal colour, habit		red, prism
Crystal dimensions [mm]		$0.20 \times 0.36 \times 0.60$
Temperature [K]		233(1)
Wavelength [Å]		0.71073
Unit cell parameters	a [Å]	7.977(2)
	b [Å]	9.713(2)
	c [Å]	16.024(3)
	α, β, γ [°]	98.03(3), 98.32(3), 113.98(3)
	V [Å^3]	1095.1(5)
$2\theta_{(max)}$ [°]		56.6
Total reflections measured		12936

Some information for full completion of the CIF is not supplied, but that is not important here.

Tasks:

Solve the structure in the usual way up to anisotropic refinement, then look at the cation geometry. Is it "normal"?

Look at contoured difference electron density maps.

Consider the displacement ellipsoids in some cation atoms and the –CF$_3$ group of the anion. Consider also if all bond angles in the cation are realistic. How much of the cation is disordered?

Another orientation of the entire cation is evident as well as disorder of the –CF$_3$ group.

A disorder model for all atoms of the cation, plus the –CF$_3$ group needs to be set up. This requires the use of constraints and restraints at various times, and we will use, among other SHELXL instructions, SAME, SADI, SIMU, possibly RIGU, PART, AFIX 66.