X-Ray Single Crystal Diffraction Practical Coursework – 5 weeks

Locations Room 1.076, Measurement Lab and X-Ray Lab 5.12

Introduction

Much of inorganic chemistry is based on reacting simple binary metal salts with organic ligands and elucidating the structure of the complexes thus formed.

$MX_x + yL \rightarrow MX_xL_y$ or $ML_y^{x+}\ xX^-$ or polymer or cluster or solvate or …….

Single-crystal X-ray diffraction is the main method of structural characterisation and requires the formation of suitable crystals. The reaction and crystallisation stages can be combined (reactive crystallisation) to enable efficient screening of a range of metal salts and ligands. The outcome is highly dependent on the choice of solvents, both in terms of the initial reaction and the quality of the final crystals. Once the crystal structure is determined, highly accurate geometric parameters are available, which enable bonding in the complex to be described. Furthermore the parameters can be compared with those of similar structures in the Cambridge and ICSD crystallographic databases in order to investigate the structural influences of changing functional groups etc.,
This Single Crystal Diffraction Practical aims to give the student experience of the steps taken to go from starting reactants to publishable crystal structure.

Course structure - For convenience the work will be written up as three reports.

(i) Applications of the Cambridge crystallographic database (CCD) and associated software (Conquest, Vista, Mercury)
(ii) Crystallisation experiments
(iii) Transforming a Crystallographic Information File (CIF) into an Acta Cryst. publication.

Mark Allocation	Cambridge	Crystallisation	CIF to Acta
Clearness of presentation, including figures and tables	10	10	20
Quality of information. Introduction, Results, Discussion and Conclusion or Abstract and Comment	15	15	30
TOTAL	25	25	50

Total marks for coursework = 100. The write-up must make it clear that student is aware of safety issues. Include a signed COSSH form and a description of radiological protection measures as appropriate.

1. Cambridge Crystallographic Database coursework (week 1)

Set up laptops. Student accounts have already been set up to access the CSD crystallographic databases at http://cds.rsc.org/.
Procedure for accessing the database including usernames and passwords will be provided by the Demonstrators.
Briefing on CCD, Conquest, Vista and Mercury.
Use Conquest to identify the type of coordinating atoms preferred by a particular metal. Each student will use Conquest and Vista to study the metal(s) and coordinating element(s) assigned by the demonstrator. Devise search parameters and fragments that will select a metal in a particular coordination and oxidation state. Determine the number of occurrences of a particular coordinating element with the metal in the database and record the average bond length. Each write-up should describe how the search was carried out in detail. Use screens captured from Vista to illustrate the report.
Demonstrators will combine all student data in Excel spread-sheets to produce histograms of the occurrence of each metal with selected ligands in common geometries in the database. The spread-sheets will be given to all students so that they can include them in their report and comment on them.

The report should include.

(a) An introduction describing the Cambridge Database, Conquest and Vista
(b) An experimental section describing how the searches were carried out in Conquest. How were the different geometries and oxidation states selected?
(c) Results section. Include numbers of hits for particular geometries and oxidation states. Also bond length means, ranges and standard deviations. Illustrate with screen captures from Vista, including captions.
(d) Discussion of results. What did you think of the search tools provided in conquest? Did they allow you to filter out the fragments you wanted? Did the variation in bond lengths with geometry and oxidation states make sense? Comment on the combined bond length information. How did the bond lengths vary with number of d electrons?

2. Crystallisation coursework (Week 2)

Briefing on crystallisation methods. Plan experiment. Which reactants? Which solvents?
Crystallisation experiment. Fill in COSSH forms. Prepare stock solutions.
Small scale, dropwise, mixing of ligands and metal salt (L1, L2, L3, M1, M2, M3) in 3 by 3 grids. Try vapour diffusion and slow evaporation. Crystallisation vessels can be left on bench on Thursdays but will have to be stored in cupboard on Friday.

Examine products using an optical microscope and make table of results (Crystals?/Powder?/Solution?/Colour?). Identify crystals that are suitable for single-crystal study. Hold a group meeting to review the crystallisations. Share data. Are certain metals better than others at producing crystals? Are certain ligands better? Vapour diffusion? Which solvent? Slow evaporation? The crystallisation part of the report will be marked out of 25. Marks will **not** be lost if unsuccessful in obtaining suitable crystals provided the experimental work was carried out correctly and the appearance of crystallisation containers reported clearly. Marks will be given for drawing sensible conclusions from the combined results.

The report should include.

(a) An introduction describing crystallisation methods.
(b) Experimental section describing how the crystallisations were carried out, ligands?, metal salts?, weights?, solvents?
(c) Results section describing colours of solutions on mixing. Were there any solids produced, colour, crystalline, shape?
(d) Discussion. Were the crystallisation methods successful? Compare with results obtained by other students. Was there a pattern?

3. Crystal Information File (CIF) to Acta Cryst. Publication (Weeks 3-5)

An unpublished CIF will be assigned to each student. These will form the basis of the final report in the form of an Acta Cryst C paper.
Start by studying the CIF using Mercury.
Construct a CHEMDRAW schematic of the molecule(s) (Use bond lengths and angles from Mercury to identify bond types).
Compare with similar structures identified using Conquest. Use Mercury and/or Vista to analyse geometric parameters. Remember to take s.u. (e.s.d.) into consideration when comparing bond lengths in your structure with those in publications.
Prepare JPEG figures showing individual molecules and packing diagrams. These can be inserted in word documents.
Edit the CIF using publCIF software in order to prepare an Acta Crystallographic C paper.
Details of what to include in the report are provided on a separate sheet.

Small groups of students will be given an opportunity to visit the X-ray Diffraction lab during the above sessions

Important. You must make sure your work is backed-up (Memory sticks, P drive).