



METHODS OF GROWING SINGLE CRYSTALS

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ABSTRACT

In the synthesis (organic, inorganic, organometallic, biochemical) crystal structure of the compound is the milestone. Any crystal structure shows - exact connectivity, bond distances, angles, complete identification of the compound, intermolecular interactions and intramolecular interactions. Information gained is rarely incorrect. It provides positive identification and answers of basic questions regarding bonding. To know the crystal structure we have to grow single crystals by using different strategies and have the idea how single crystals grow from solid, liquid and gas phase.

KEYWORDS: Crystal growth, single crystal, data collection, structure refinement

INTRODUCTION:

Single crystal X-ray crystallography is one of the most popular analytical methods. Many Scientists discovered structures of valuable molecules like DNA, cholesterol and vitamin B12 etc by using this technique. The determination of a crystal structure consists of several steps: crystal growth, unit cell determination, data collection, data reduction, space group determination and structure solution, following these steps the crystallographer obtain atomic coordinates for some or all non-hydrogen atoms. These steps from unit cell determination to structure solution collectively called refinement [1-7].

In this paper we are describing different techniques to grow single crystals and Importance of the single crystal X-ray crystallography.

IMPORTANCE OF SINGLE CRYSTAL X-RAY CRYSTALLOGRAPHY (SCXRC)

Many researchers involves in the synthesis of compounds and determination of structure is a key goal, for the determination of structure they use many spectroscopic techniques like IR (Infrared spectra), NMR (Nuclear magnetic resonance) and Mass spectroscopy etc but these techniques do not provide the sharp information about the structure of the compound. Therefore to know the systematic structure we use SCXRC. Crystal structure provides: (i) Confirm Structure (iii) Exact connectivity (iv) Bond distances and angles (v) Complete identification of the compound (vi) Intermolecular and interactions (vii) Comparison of SCXRD and PXRD can confirm that crystal is representative of bulk, etc.

Till to date 29 Nobel prizes have been given in the field of X-ray crystallography and related field [8].

METHOD TO OBTAIN SINGLE CRYSTALS [9, 10]

Single crystal produced by the transport of crystal constituent in solid, liquid or vapour phase. Crystal growth can be divided into three categories-

- I. Solid Growth – Solid to solid phase transformation
- II. Liquid Growth – Liquid to solid phase transformation
- III. Vapour Growth – Vapour to solid phase transformation

Although there are many techniques to grow the single crystals but scientists mainly use the following three strategies.

- (i) Vapour diffusion
- (ii) Layering
- (iii) Slow evaporation

Before using any of the above methods to grow single crystals we need to have pure solid samples. Therefore solid materials must be recrystallize properly (Table 1) and other important things are-glassware should be clean, consider proper location and volume needed to grow the crystals. Then try to grow fine single crystals.

(i) VAPOUR DIFFUSION:

This method is most popular among synthesis community and crystallographers. To grow the crystal by this method we need milligram amounts of compound and solvents. For diffusion, we need to be aware of vapor pressures of solvents. Have available a chart of physical properties of solvents (Table 1 and 2)

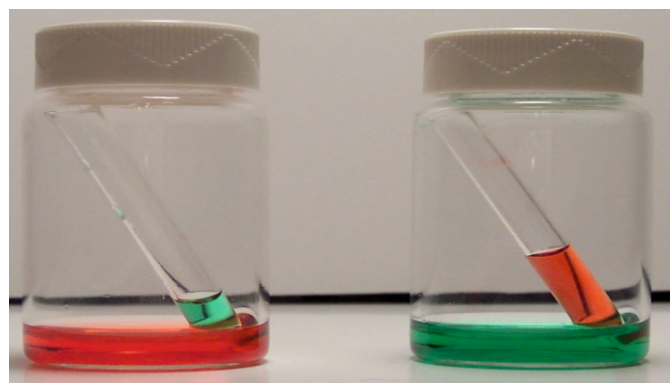


Fig 1: Showing vapour diffusion method for single crystal growing

We always take filtered, less volatile solvent solution of compound inside the tube (inner vessel) and more volatile solvent outside in the tube in the chamber as shown in figure 1.

Compound should not be soluble or less soluble in the more volatile solvent that is outer solvent. When vapours of more volatile solvent enter in the tube, containing compound solution then compound starts to precipitate slowly. This slow precipitation leads to grow crystals inside the tube.

Mostly chamber placed in cool place where nobody disturbs the chamber. Grown single crystals can be seen by using white torch light or laser light without disturbing or touching the chamber.

LAYERING

Layering can be done in the NMR, or glass tube (as shown in figure). It must be very careful ([Fig 2]).



Fig 2: Showing layering tube and crystal structure obtained by layering method

The bottom solvent must be of higher density (Table 2) and compound can be soluble in one of the solvent and partially or insoluble in other solvent and these two solvent must be fully miscible with each other. When these solvent, one containing compound, carefully layered with each other and placed in cool place then they starts to mix together and compound starts to precipitate slowly. This slow precipitation grow the crystals on the walls of layering tube.

SLOW EVAPORATION

Generally most of the compounds crystallize out by this method and this is the easiest method among all methods. First step is- filter to remove any particles and allow the material to crystallize out as the solvent evaporates. Keep the solution clean and covered to avoid dust particles (Figure 3).



Fig 3: Representation of slow evaporation method

Place the setup in cool place without any disturbance for longer time, sometimes it takes more than a month

RESULT AND DISCUSSION

By following above methods one can grow fine crystals which can be diffracted and crystal data can be collected using single crystal X-ray diffractometers

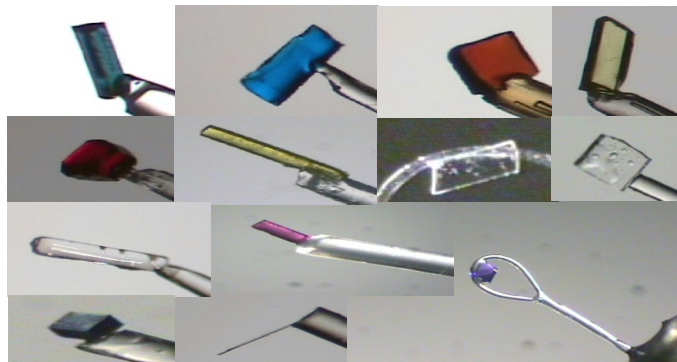


Fig 8: Showing single crystals obtained by different methods

The crystal data can be solve by using different freely available software like WingX, Olex2, and SHELXTL etc. After solving the data carefully one can store his data in the Cambridge Crystallographic Data Centre (CCDC) which is a data base of crystal structures.

While publishing the crystal structure authors have to provide CCDC number in the paper so that referees can obtain the data to check it.

Table 1. Solvent combination using in different methods

Method	Solvent and Combination	
	CH ₃ CN	CH ₂ Cl ₂
Recrystallization	CH ₃ CN + EtOH (1:5) CH ₃ CN + Hexane (2:1) CH ₃ CN + Et ₂ O CH ₃ CN + DMF (2:1) CH ₃ CN + Toluene (2:1)	CH ₂ Cl ₂ – Hexane CH ₂ Cl ₂ – Et ₂ O CH ₂ Cl ₂ – MeOH CH ₂ Cl ₂ – Toluene
Slow Evaporation	CH ₃ CN + EtOH CH ₃ CN + CH ₂ Cl ₂ CH ₃ CN + THF	
Vapour Diffusion	CH ₃ CN – Et ₂ O CH ₃ CN – EtOAc CH ₃ CN + MeOH(1:1) – Et ₂ O CH ₃ CN + MeOH(1:1) – MeOH CH ₃ CN + Toluene/ Et ₂ O CH ₃ CN + THF/ Et ₂ O	
Layering	CH ₃ CN – Toluene CH ₃ CN – Benzene CH ₃ CN – THF CH ₃ CN + CH ₂ Cl ₂ – THF	CH ₂ Cl ₂ – Hexane CH ₂ Cl ₂ – Pentane CH ₂ Cl ₂ – Heptane CH ₂ Cl ₂ + Toluene – Hexane CH ₂ Cl ₂ – Et ₂ O CH ₂ Cl ₂ + Acetone – Hexane CH ₂ Cl ₂ – Pet ether

	CH ₃ OH	Acetone
Recrystallization	MeOH + CH ₂ Cl ₂ (1:2) MeOH + H ₂ O (1:1) MeOH + MeCN (2:1)	Acetone + H ₂ O Acetone + 2- propanol (1:1)
Slow Evaporation	MeOH + THF	
Vapour Diffusion	MeOH – Et ₂ O MeOH + H ₂ O – Et ₂ O MeOH + CH ₃ COCH ₃ /Et ₂ O	Acetone /Et ₂ O
Layering	MeOH – Toluene MeOH – Benzene	Acetone – Hexane Acetone – Heptane Acetone – Pentane Acetone – CH ₂ Cl ₂

	DMF	CHCl ₃	THF
Recrystallization	Isopropanol + DMF +MeOH (2:1:1)	CHCl ₃ – Hexane	THF–Et ₂ O
Vapour Diffusion	DMF – Et ₂ O DMF – MeOH DMF – CH ₃ COCH ₃ DMF + MeOH (1:1) – Et ₂ O	CHCl ₃ - Et ₂ O	THF– Acetone
Layering	DMF – isopropanol	DMF – Et ₂ O	

Table 2. Densities and boiling points of solvents

Solvent	Density	Boiling Points(°C)
CH ₂ Cl ₂	1.32	41
Acetone	0.78	56
CHCl ₃	1.49	61
MeOH	0.79	65
THF	0.88	66
Hexane	0.65	69
EtOH	0.78	78
EtOAc	0.89	78
Benzene	0.87	80
CH ₃ CN	0.78	82
Toluene	0.86	111
DMF	0.94	155

CONCLUSIONS

In this paper we have explained how to grow fine crystals by using most popular methods. We have described importance of single crystals we also provided very useful table containing physical parameters for recrystallization and single crystal growing.

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