

## 2. Method of study

### 2.1 Chemicals

#### 2.1.1 Materials from Fluka AG, Switzerland

*N*-Phenylthiourea, C<sub>7</sub>H<sub>8</sub>N<sub>2</sub>S, purum

Copper(I) bromide, CuBr, L.R. grade

Copper(I) chloride, CuCl, L.R. grade

#### 2.1.2 Materials from Lab-Scan

Ethanol, C<sub>2</sub>H<sub>5</sub>OH, A.R. grade

Acetonitrile, CH<sub>3</sub>CN, A.R. grade

#### 2.1.3 Materials from Aldrich Chemical Company, Inc.

Copper(I) iodide, CuI, L.R. grade

### 2.2 Instruments

2.2.1 Capillary Melting Point Apparatus, Thomas Hoover, Unimelt 0 – 360 °C

2.2.2 UHU Epoxy Adhesive

2.2.3 Bee Wax

2.2.4 Fiber Glass, 0.1 – 0.4 mm (diameter)

2.2.5 Thermometer, Gallenkamp, England 0 – 360°C

2.2.6 Hot plate stirrer with magnetic bar

2.2.7 Infrared spectra were recorded with either Perkin Elmer Spectrum GX

2.2.8 Spectrace 5000 X-ray Fluorescence

2.2.9 Bruker SMART APEX CCD Diffractometer

## 2.3 Preparation of complexes

### 2.3.1 Preparation of $[\text{Cu}(\text{ptu})_4]\text{Cl}$ complex

*N*-Phenylthiourea (2.30 g, 15 mmol) was dissolved in acetonitrile (60 mL) at 50°C with continuous stirring. CuCl (0.5g, 5 mmol) was slowly added and the solution was kept warm for 5 h, after which time it was filtered and allowed to cool to room temperature. Slow evaporation of this solution yielded colorless crystals. They were isolated by suction filtration and washed with acetone before being dried in a vacuum desiccator.

### 2.3.2 Preparation of $[\text{Cu}_4(\text{ptu})_6\text{Br}_4]_2$ complex

*N*-Phenylthiourea (1.60g, 10 mmol) was dissolved in acetonitrile (60 mL) at 60°C. Then CuBr (0.5g, 3.5 mmol) was slowly added with continuous stirring for 4 h. After that it was filtered and allowed to cool to room temperature. Slow evaporation of the solvent yielded colorless plate crystals. They were isolated, washed and dried as in 2.3.1

### 2.3.3 Preparation of $[\text{Cu}_4(\text{ptu})_6\text{I}_4]_2$ complex

*N*-Phenylthiourea (1.19 g, 2.6 mmol) was dissolved in acetonitrile (60 mL) at 60°C with continuous stirring. CuI (0.5 g, 7.8 mmol) was slowly added and the solution was kept warm for 4 h, after which time it was filtered and the filtrate then left at room temperature. After 2 days, the solution yielded colorless plate crystals. They were isolated by suction filtration and washed with acetone before being dried in a vacuum desiccator.

## 2.4 Methods for Determination Structures

### 2.4.1 X-ray Fluorescence Technique

Cu, S and halides (Cl, Br and I) qualitative analyses of [Cu(ptu)<sub>4</sub>]Cl, [Cu<sub>4</sub>(ptu)<sub>6</sub>Br<sub>4</sub>] and [Cu<sub>4</sub>(ptu)<sub>6</sub>I<sub>4</sub>] were performed by X-ray fluorescence spectrometer (PerkinElmer, PW2400).

### 2.4.2 Infrared Spectroscopy (IR)

Infrared spectra in the region 4000 – 400 cm<sup>-1</sup> were measured on a Perkin-Elmer 783 Infrared Spectrophotometer and Perkin-Elmer Spectrum GX FTIR-spectrophotometer using potassium bromide disc.

### 2.4.3 CHNS Analysis

Carbon, hydrogen, nitrogen and sulfur contents in the synthetic crystals were determined by CE Instruments Flash 1112 Series EA CHNS-O Analyser.

### 2.4.4 Crystal Structure Determination by Single Crystal X-ray diffraction Techniques

The structures of the synthesized crystals were determined by following steps in Figure 8.

Figure 8 shows an outline of crystal structure determination in a simplified form as a schematic flowchart. The involved steps are in the boxes. To the right of each is listed the information obtained and to the left an indication of the time-scale involved in carrying out the operation. Some of these times vary considerably, depending on the quality of the sample being studied, the resources

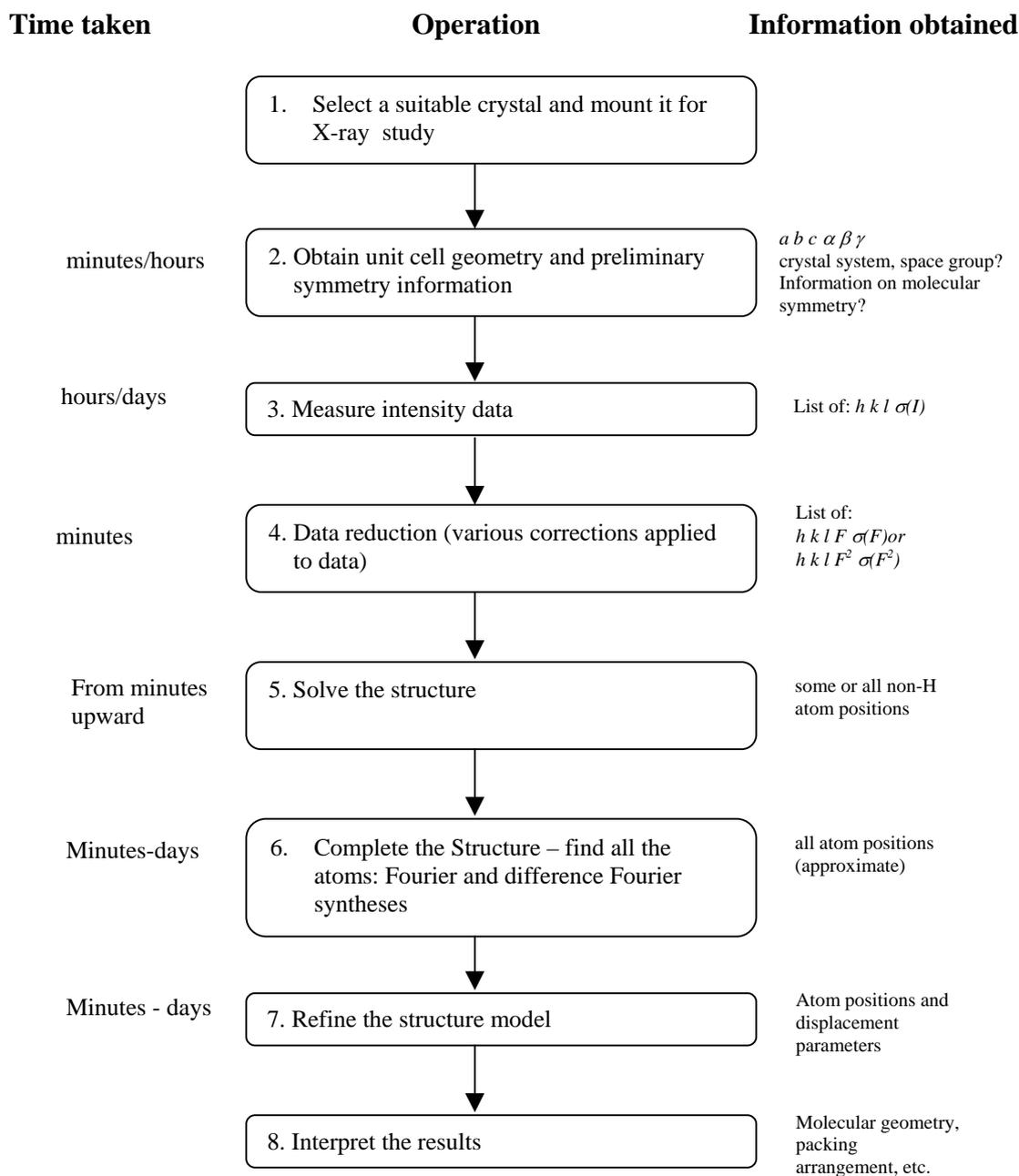


Figure 8 A flowchart for the steps involved in a crystal structure determination.

available for the work, the size and complexity of the structure, the skill of the crystallographer, and a certain amount of luck.

## 1. Selection of a suitable crystal and mounting it for X-ray study

### 1.1 Crystal selection

The following lists are the requirements of a nice crystal which would be fulfilled. In practice there are not so many choices available. A batch of crystals comes as is. Nevertheless it may bear these remarks in mind when select the most appropriate crystal.

- Select a crystal with a size around 0.2 - 0.3 mm for organic compounds. Use smaller sizes for compounds containing heavier atoms to reduce the absorption effects. Crystal sizes in general can be selected smaller than on a conventional serial diffractometer. Since crystal size is related to spot size, you will have less overlap from smaller crystals.
- Select a crystal with a simple, regular shape.
- Check crystals under a polarizing microscope. A good single crystal will extinguish completely on a distinct position when between crossed polarization filters.
- Scan crystals with the Apex CCD, i.e. make a few quick exposures and check the images visually on spot shape, spacing and distribution.

### 1.2 Crystal mounting

For single crystal diffractometry it is convenient to have the crystal mounted so that it can be moved for proper alignment and centering in the camera. Crystals need to be mounted in such a way that they can be manipulated in various

devices used for intensity measurement. Two methods are commonly used to mount crystals :

(1) Crystals, not volatile or sensitive to the environment, are glued onto a thin glass fiber with an epoxy glue (Figure 9). All crystals were mounted by this method.

(2) Crystals, air-sensitive or degradable by loss of loosely bound solvents, require special treatment. They may be sealed in thin-walled glass capillary tubes. Alternatively, the crystals can be coated with an inert viscous oil and then manipulated without difficulty under a normal microscope in the open atmosphere.

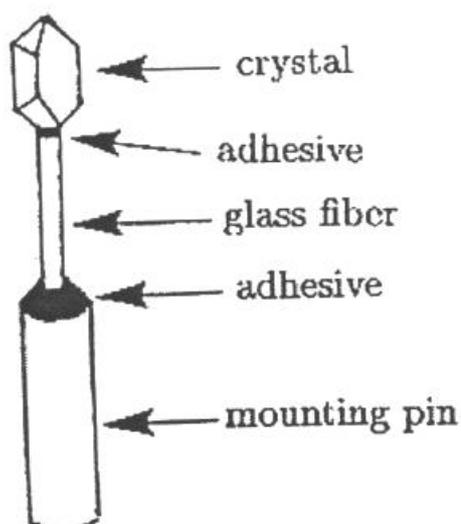


Figure 9 Crystal mounting.

## 2. Data collection

### 2.1 Data collection by film method

Diffracted X-ray can be recorded on photographic film by the Enraf Nonius FR550 Weissenberg camera into two methods.

### 2.1.1 Oscillation methods

A crystal is oscillated in the range  $10 - 20^\circ$  but without moving a film. Usually an exposure of 1 – 2 h. is enough. After exposure the film is developed, fixed and washed.

Oscillation photographs are generally used to align crystals and to measure the cell edge along axis of rotation.

### 2.1.2 Weissenberg methods

The film holder is engaged on the worm screw that leads from the motor to the crystal mounting and is moved in strict coincidence with the crystal rotation. At either end of its travel the film holder (or an adjustable stop) strikes a reversing switch, which changes the direction of the crystal rotation and sends the film back the other way. The usually free translation of the film carriage is 100 – 110 mm, corresponding to an oscillation range of  $200 - 220^\circ$ . An exposure is about 24 – 28 h. After exposure the film is developed, fixed and washed.

The cell parameters ( $a$ ,  $b$ ,  $c$ ,  $\alpha$ ,  $\beta$  and  $\gamma$ ) and space group were obtained from improving Weissenberg photographs.

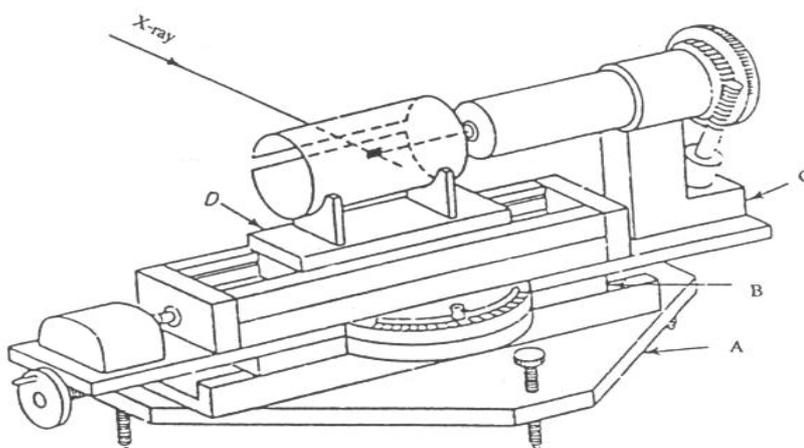


Figure 10 The Weissenberg camera.

## 2.2 Data collection by diffractometer

Diffractometer, available in various designs, is the machine used to collect X-ray data. Traditionally, four-circle diffractometers have four axes about which the crystal may be rotated ( $\phi$ -,  $\omega$ - and  $\chi$ - circle) plus the circle about which the detector can be rotated ( $2\theta$ - circle). With one of these four-circle diffractometers reflections (positions and the intensities) are measured one at a time, the crystal and detector being moved under computer control. Recently, X-ray diffractometers have become which record over a considerably larger area and are position-sensitive. Many of diffracted beams can be recorded at the same time. Modern single crystal diffractometers are now exclusively fitted with area detectors. They operate very much like a digital photographic camera but record X-ray information instead of visible light. These detectors are also very sensitive and are thus suited to small crystals in which only weak X-ray scattering can be recorded. An area detector can replace the traditional scintillation of four-circle diffractometer. The size of the area detector is large and the rotation axes are also possible to fix the  $\chi$  rotation axis because it is no longer necessary to bring all reflection into the horizontal plane in order to record data. In this work the type of detector used is a charge coupled device (CCD) detector with a three-circle diffractometer. This typical three-circle diffractometer has two axes ( $\phi$ ,  $\omega$ ) about which the crystal may be rotated plus the circle ( $2\theta$ ) about which the detector is rotated. A typical area detector and SMART APEX CCD X-ray are shown in Figure 11.



Figure 11 The SMART APEX CCD X-ray diffractometer.

The colorless crystals of  $[\text{Cu}(\text{ptu})_4]\text{Cl}$ , and  $[\text{Cu}_4(\text{ptu})_6\text{I}_4]$  were used for the data collections at room temperature (298 K) on SMART 1000 CCD (Charge Coupled Device) system by Dr. Narongsak Chaichit, Department of Physics, Faculty of Science, Thammasat University. The colorless crystal of  $[\text{Cu}_4(\text{ptu})_6\text{Br}]$  was used for the data collection at low temperature (100 K) on a 3-axis Goniometer Module D8 Advanced diffractometer, which has a SMART APEX detector with graphite monochromated  $\text{MoK}_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at Department of Chemistry, Faculty of Science, Prince of Songkla University.

The standard SMART APEX system uses a horizontally oriented D8 PLATFORM goniometer base (with 2-theta  $[2\theta]$  and omega  $[\omega]$  drives) with dovetail

tracks for the X-ray source and the detector, and mounting posts for accessories such as the video camera and optional low temperature attachment. The system also incorporates a fixed chi stage with chi angle of approximately  $54.74^\circ$  and a phi drive with  $360^\circ$  rotation as shown in Figure 12.

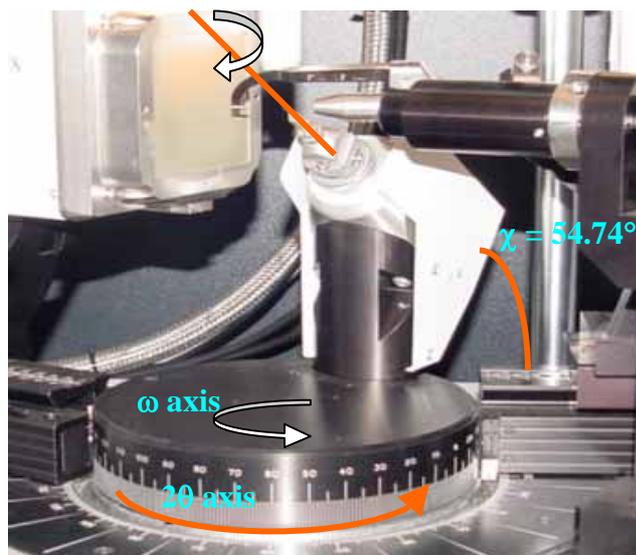


Figure 12 a 3-axis goniometer.

After crystal mounting, the crystal has to be aligned in the center of the X-ray beam. The alignment process combines optical alignment steps with rotational photo steps. During optical alignment, the goniometer head adjustment screws must be adjusted on 3 axis (X, Y and Z axis) until the crystal is on the crosshairs intersection as shown in Figure 13 and 14.

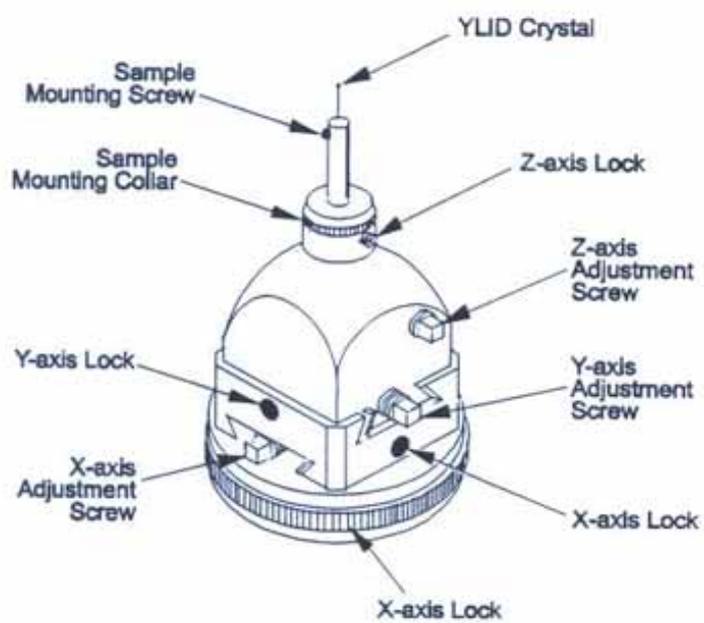


Figure 13 Goniometer head adjustment locations.

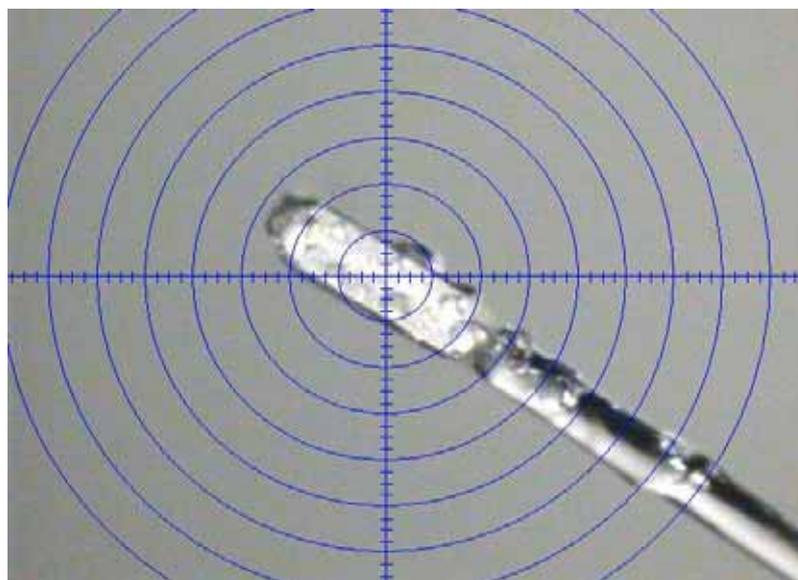


Figure 14 Crystal center on crosshairs ( $\phi = 90^\circ$ ).

SMART will then perform a 60-second rotation photo as shown in Figure 15. After that, The program collects three sets of 25 frames called MATRIX0, MATRIX1 and MATRIX2. When all frames have been collected, SMART performs the steps of thresholding, indexing, Bravais lattice determination, and least-squares refinement of cell constants.

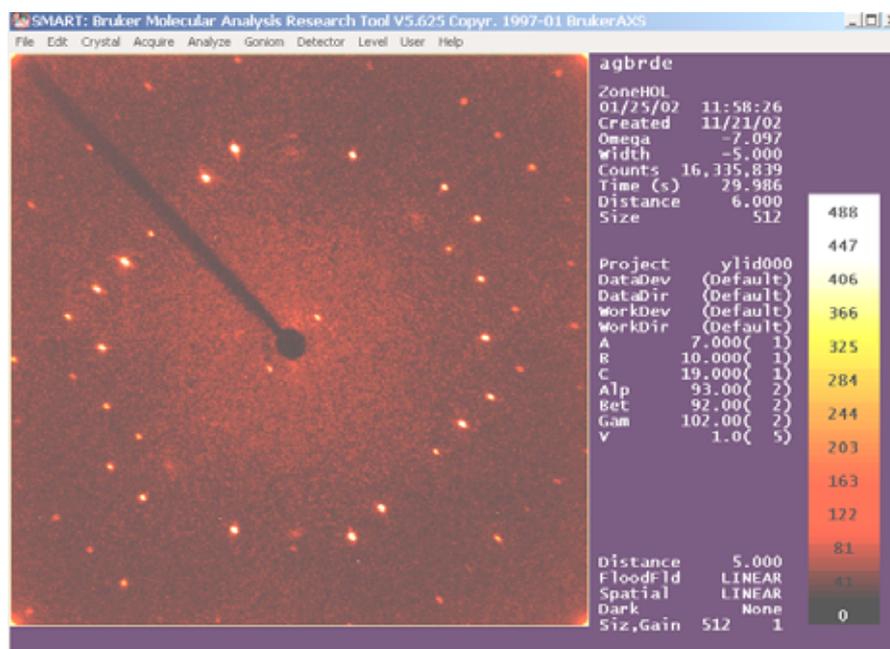


Figure 15 Image frame following 60-second rotation.

### 3. The measurement of intensities

A list of reflections, usually thousands of them,  $hkl$  indices and a measured intensity were obtained from this stage. In addition, from diffractometer measurements, each intensity  $I$  has an associated standard uncertainty,  $\sigma(I)$ , which is calculated from the known statistical properties of the X-ray generation and diffraction processes, and is a measure of the precision or reliability of the measurement.

#### 4. Data reduction

The procedure followed to extract relative structure factor amplitudes from raw integrated intensities which is called data reduction. In data reduction the different reflection dependent parameters are taken into account by multiplying the relative intensities by suitable correction factors. The intensities of an X-ray beam is proportional to the square of the wave amplitude ( $I(hkl) \propto |F(hkl)|^2$ ). The measured intensity is affected by various factors such as Lorentz ( $L$ ), polarization ( $P$ ) and absorption corrections ( $T$ ) factors. However, for which corrections must be applied. The conversion of intensities  $I$  to observed structure amplitudes  $|F_o|$  ( $o =$  observed) or  $F_o^2$  and correspondingly,  $\sigma(I)$  to  $\sigma(F_o)$  or  $\sigma(F_o^2)$  is known as data reduction and has several components.

The result of this whole process, which usually takes only a matter of minutes on computer, is a list of reflections as  $h, k, l, |F_o|, \sigma(F_o)$  [or  $h, k, l, F_o^2, \sigma(F_o^2)$ ].

#### 5. Solving the structure

After data reduction, the structures were solved by using the program Xtal 3.6 (Hall, S.R., *et al.* 1995, 1999) on UNIX workstation computer and PC at Department of Chemistry, Faculty of Science, Prince of Songkla University.

Most Xtal calculations are initiated, and controlled, from an input line file usually known as the .dat file. The results of a calculation are output to files and a screen device (as in graphics applications). Xtal calculations use various files to store intermediate and archival data. This strong dependence on files means that Xtal is considered a file-driven archival system, rather than an interactive menu-driven system.

The convention for filename construction for all Xtal files is normally <compid><ext> where compid is the compound identification code (maximum of six characters), and ext is the extension code (three characters). The compid code is defined by the user at the start of the input commands with the line “compid”.

The steps in solving structure by Xtal program are as follows.

1. Getting started

This step is generating binary data files, that are used as working files, and to archive certain types of data. The subprograms for this step are

STARTX : Create initial archive file

ADDREF : Add reflection data

SORTRF : Sort and merge reflection data

2. Solving the structure

Heavy atom methods was used to solve the structures for this work. This method involve solving structure of compounds that have heavy atoms. The subprograms for this step are

GENEV : Normalized structure factors ( E values)

FOURR VECT: Patterson fourier map

PEKPIK : Search for peaks in map

3. Refining the structures

Once all atoms have been found, the model structure needs to be refined.

This means varying the numerical parameters describing the structure to produce the best agreement. Anisotropic thermal parameters are used for all non-hydrogen atoms. Hydrogen atoms were located in difference-Fourier analyses and included with coordinations refined.

The refinement process uses a well-established mathematical procedure called least-squares analysis, which define the best fit of two sets of data (here  $|F_o|$  and  $|F_c|$ ) to be that which minimize one of the least-squares sums :

$$\sum w (|F_o| - |F_c|)^2$$

- $w$  = Reflection weights  
 $F_o$  = Observed structure factors  
 $F_c$  = Calculated structure factors

The subprograms for this step are

ADDATM : Load atom parameters

CRYLSQ : Structure factor least-squares refinement

#### 4. Checking geometry

This step is checking the structure. If atoms of the model structure are approximately in the right positions, there should be at least some degree of resemblance between the sets of calculated structure factors,  $|F_c|$  and observed structure factors,  $|F_o|$ . This is the most widely used assessment which is a so-called residual factor or *R*-factor, defines as

$$R = \frac{\sum \left| |F_o| - |F_c| \right|}{\sum |F_o|}$$

$$R_w = \sqrt{\frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2}}$$

For a correct and complete crystal structure determination from well measured data,  $R$  is typically around 0.02 – 0.05 or 2 – 5 %. Values of  $R_w$  based on  $|F|^2$  are generally higher than those base on  $|F|$  values. The subprograms for this step are

CRYLSQ

BONDLA : Bond lengths and angles

#### 5. Preparing for publication

This step is showing the results by pictures and numerical parameters for report and publishing. The subprograms for this step are

LISTPF : List formatted reflection data

LSQPL : Least-squares planes & lines

ORTEP : Molecular plot

PLOTX : Interface plot devices

ATABLE : Tabulate atomic parameters