

2. Method

2.1 Chemicals

Products of Fluka Chemical, Buchs, Switzerland

1. *N,N'*-Ethylenethiourea, $C_3H_6N_2S$, purum
2. *N,N'*-Diethylthiourea, $C_5H_{12}N_2S$, purum
3. Copper(II) acetate monohydrate, $Cu(CH_3COO)_2 \cdot H_2O$, purum

Products of E.Merck, Darmstadt, Germany

1. Copper(II) nitrate trihydrate, $Cu(NO_3)_2 \cdot 3H_2O$, purum

Products of Aldrich Chemical Co., Inc., USA

1. Copper(II) perchlorate hexahydrate, $Cu(ClO_4)_2 \cdot 6H_2O$, L.R.grade

Products of Lab-Scan Analytical Science

1. Ethanol, C_2H_5OH , A.R.grade
2. Acetone
3. Acetonitrile
4. Methanol, CH_3OH , A.R.grade
5. Dimethylsulfoxide

2.2 Preparation of Complexes

Copper oxyanion complexes containing *N,N'*- ethylenethiourea and *N,N'*- diethylthiourea have been prepared by many ways, for instance, varying mole ratios of reactants, solvents, reaction time and reaction temperature. However, there were 4 complexes the crystals of which were suitable to be studied by X- ray diffraction method. The following particular is about the methods of crystal preparation of these complexes.

2.2.1 $[\text{Cu}(\text{etu})_3]_2\text{SO}_4$

$\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (0.25 g, 1.25 mmol) was added to *N,N'*-ethylene thiourea (0.32 g, 3.13 mmol) in distilled water (50 mL) at 80 °C with continuous stirring for 5 h. After which time the initially light blue reaction mixture became green, this was then cooled to room temperature. Slow evaporation of solvent at room temperature for 3 days yielded colorless prismatic crystals. They were removed by filtration and vacuum dried over silica gel.

2.2.2 $[\text{Cu}_2(\text{detu})_6](\text{NO}_3)_2$

$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.25 g, 1.03 mmol) was added to *N,N'*-diethylthiourea (0.41 g, 3.10 mmol) in distilled water (50 mL) at 60 °C with continuous stirring for 6 h. The initially white solution gradually changed to light blue leaving a light yellow microcrystalline solid. Then it was filtered and allowed to stand at room temperature. From the remaining solution, the colorless prismatic crystals obtained within 2 days by slow evaporation at room temperature and removed by filtration and vacuum dried over silica gel.

2.2.3 $[\text{Cu}(\text{detu})_3]_2 \text{SO}_3$

$\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (0.50 g, 2.50 mmol) was added to *N,N'*-diethyl thiourea (1.0 g, 9.08 mmol) in distilled water (100 mL) at 55 °C with continuous stirring for 6 h. During this addition, the solution exhibited a cloudy white color. Then the colorless solution was filtered and allowed to stand at room temperature. After filtration and remaining solution was slowly evaporated at room temperature within 11 days, a small amount of colorless prismatic crystals were obtained. Removed the crystals from the resultant solution by filtration and vacuum dried over silica gel.

2.2.4 $[\text{Cu}_2(\text{detu})_6](\text{ClO}_4)_2$

$\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.50 g, 1.35 mmol), dissolved in minimum quantity of distilled water (10 mL), was added slowly with continuous stirring to a preheated solution of *N,N*-diethylthiourea (0.54 g, 4.08 mmol) in 50 mL of acetonitrile - ethanol (50 : 50, vol. / vol.) at 50 °C. The black solution became colorless immediately. After 5 h., the resulting solution was allowed to stand at room temperature and after slowed evaporation for 4 days giving yellow prismatic crystals of S_8 which were collected by filtration. The filtrate was slowly evaporated at room temperature for 2 days yielded colorless needle crystals and removed from the resultant solution by filtration and vacuum dried over silica gel.

2.3 Melting Point Measurement

Melting point of the complexes were measured on Capillary Melting Point Apparatus, Thomas Hoover, Unimelt 0 - 360 °C.

2.4 X - ray Fluorescence Spectrometry

Copper and sulfur qualitative analyses were performed by EDXRF techniques on X - ray Fluorescence Spectrometer PW 2400.

2.5 Infrared Spectroscopy

Infrared spectra of ligands and complexes were measured on a Perkin Elmer Spectrum GX FT - IR spectrometer in the range 4,000 - 400 cm^{-1} . All samples were prepared in the KBr pellets.

2.6 Elemental Analysis

Elemental analyses were measured by CE Instruments Flash 1112 Series EA CHNS - O Analyser.

2.7 Single crystal X - ray diffractometry

The crystallographic data of $[\text{Cu}(\text{etu})_3]_2\text{SO}_4$ was collected using Seimens SMART CCD at Thammasart University by Dr. Narongsak Chaichit. The crystallographic data of $[\text{Cu}_2(\text{detu})_6](\text{NO}_3)_2$ was collected using SMART CCD detector system at University of Western Australia, Australia by Prof. Dr. Allan H. White. The crystallographic data of $[\text{Cu}(\text{detu})_3]_2\text{SO}_3$ and $[\text{Cu}_2(\text{detu})_6](\text{ClO}_4)_2$ and S_8 were collected using Bruker APEX CCD X - ray diffractometer system at Department of Chemistry, Prince of Songkla University.

A typical X - ray diffraction experiment consists of following of the steps :

- Growth some crystals.
- Select and mounted a suitable crystal for X - ray study.
- Collect X - ray scattering data.
- Solve and refine structure.
- Interpret the results.

2.7.1 Crystal growth

Normally crystals are grown from a solution and growth should be as slow as possible to allow regular arrangement of the molecules or ions to produce a well- defined crystal.

2.7.2 Select and mount a suitable crystal

For X-ray work on modern diffractometers, the crystal must be of suitable dimension not smaller than 0.1 mm, and not larger than 0.4 mm, for fully bathed in X-ray beam. Because of the large crystals containing strongly absorbing elements may also absorb more X-ray than they diffract. Furthermore the crystal must possess a regular repeating pattern as a single crystal.

In crystal mounting, it is convenient to have the crystal mounted so that it can be moved for proper alignment and centering in the X-ray beam. Normally, the crystal is glued onto a thin glass fiber with an epoxy glue as shown in Figure 38.

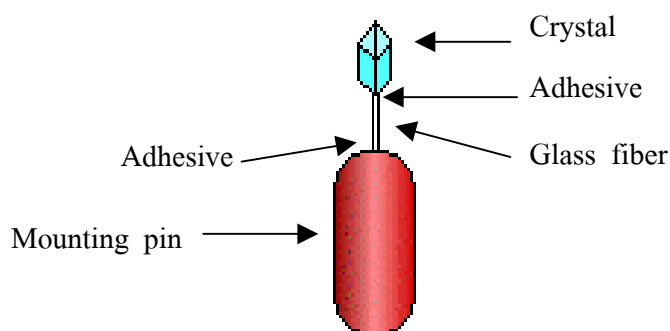


Figure 38. Crystal mounting.

The mounted crystal was attached to a goniometer head as shown in Figure 39., this device holds the crystal in place on a goniometer and allow it to be oriented in the X-ray beam by means of translational and angular motions.

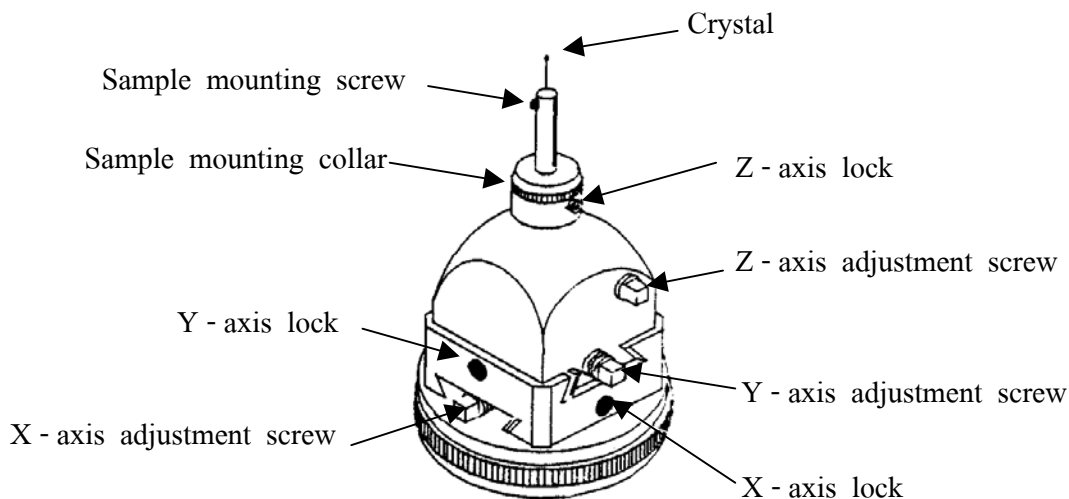


Figure 39. Goniometer head adjustment locations.

2.7.3 Data collection

2.7.3.1 X - ray photography

The Enraf Nonius FR 500 Weissenberg camera was performed, 2 methods of X-ray photography have been used :

(1) Oscillation method

A crystal is oscillated over a range of $10 - 20^\circ$ but without moving a film. Usually, an exposure of 1 - 2 h. is sufficient. After exposure the film is developed, fixed and washed. Oscillation photographs are generally used to align crystals and to measure the cell edge along the axis of rotation.

(2) Weissenberg method

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 strikes a reversing switch, which changes the direction of the crystal rotation and sends the film back

the other way. The usual free translation of film carriage is 100 - 110 mm., corresponding to an oscillation range of $200 - 220^\circ$. An exposure is about 24 - 48 h. After exposure the film is developed, fixed and washed.

Weissenberg photographs can be used for improving alignment, measuring cell contents ($a, b, c, \alpha, \beta, \gamma$) and determining the space group. The picture of Weissenberg camera and X-ray photography are shown in Figure 40 - 41.

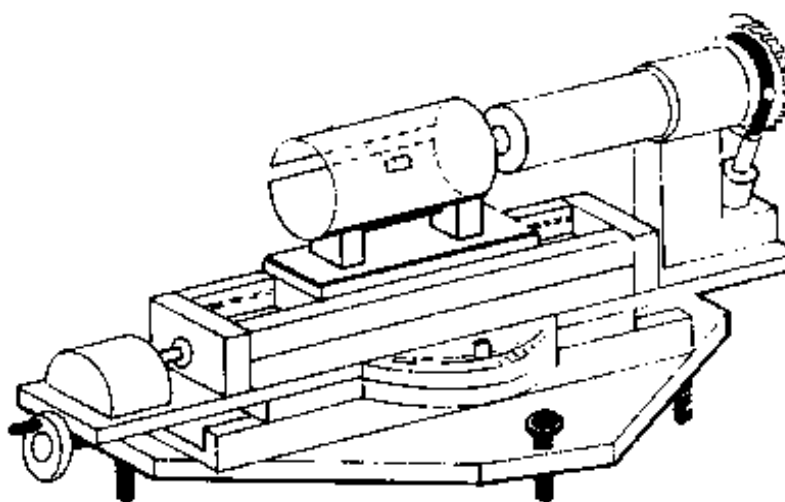


Figure 40. The Weissenberg camera.

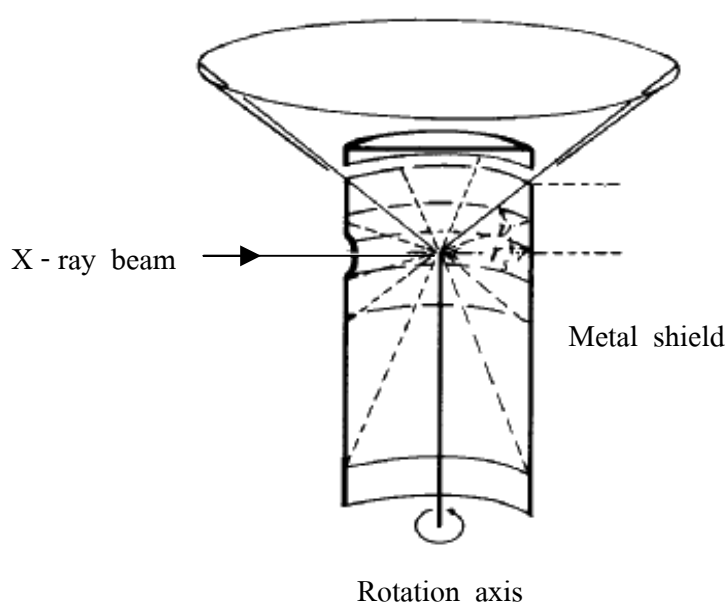


Figure 41. X-ray diffraction on a film.

2.7.3.1 X - ray diffractometer

The SMART APEX system as shown in Figure 42., consists of the following basic components.

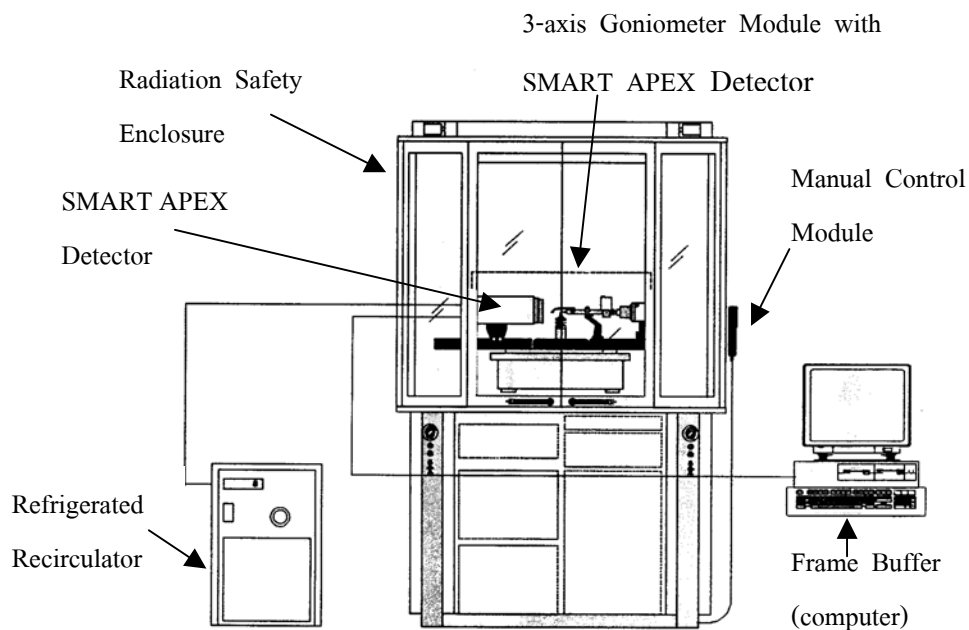


Figure 42. SMART APEX system components.

(1). 3 - axis goniometer module with SMART APEX components

The 3 - axis goniometer module and its associated SMART APEX detector comprise the unique hardware of the SMART APEX system. Several components comprise the 3 - axis goniometer module with SMART APEX detector as shown in Figure 43.

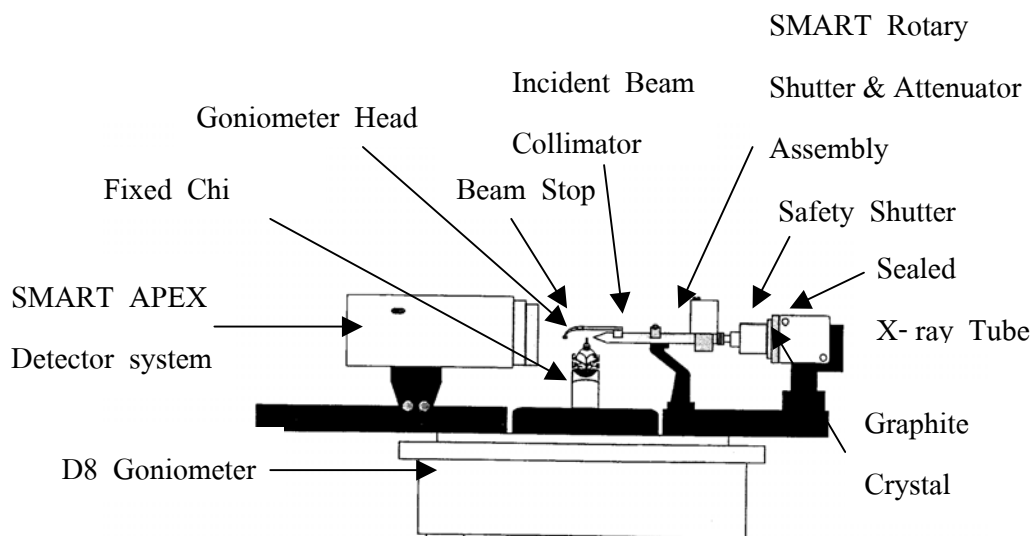


Figure 43. SMART APEX and goniometer module instrumentation.

Goniometer with fixed chi stage

The standard SMART APEX system uses a horizontally oriented D8 PLATFORM goniometer base 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° and phi drives with 360° rotation. All four axes (2θ , ω , ϕ and χ) intersect within a volume of approximately 10 microns. These axes are shown in Figure 44.

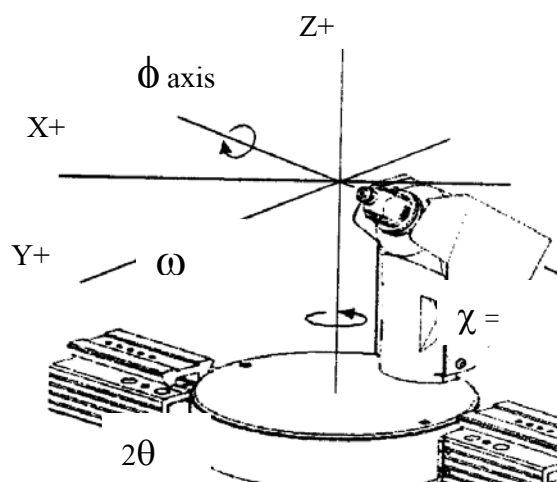


Figure 44. Fixed χ , 3 - axis goniometer.

X - ray source

Three components in Figure 43. comprise the X - ray source : a shielded X - ray tube, an X - ray safety shutter, and a graphite crystal monochromator. The sealed tube X - ray source with a molybdenum (Mo) target produces the X - ray beam used by the SMART APEX system. The X - ray safety shutter is built into the X-ray tube shield. The shutter opens upon initiation of a set of exposures and closes upon the end of collection. Status lamps on the shutter housing indicate when the shutter is open and close. The shutter is also interfaced to the controller and to the safety interlocks. A tunable graphite crystal monochromator selects only the K_{α} line ($\lambda = 0.71073 \text{ \AA}$) emitted from the Mo X - ray source and passes it down the collimator system.

SMART rotary shutter and collimator

The monochromatic X- ray beam then passes through the SMART rotary shutter, and the incident beam collimator before striking the specimen. The entire collimator assembly is supported by a collimator support assembly which has been precisely aligned to guarantee that the X - ray beam passes through the center of the goniometer.

AMART APEX detector

The SMART APEX detector is specific to this system. It is mounted on a 2θ dovetail track. The track has a scale that is calibrated to indicate the distance from the crystal to the phosphore window.

K760 X - ray generator

The K760 generator is a high frequency, solid - state X - ray generator, which provides a stable source of power for operations up to 60 kilovolts (kV) and 50 milliamps (mA). For the SMART APEX system, power settings should never exceed the maximum power rating of the X - ray tube.

Typical maximum power settings for the SMART APEX system with a normal focus tube are 50 kV, 40 mA.

Manual control module

The manual control module is a remote device that will use in certain operations to manually drive angles.

Video camera

The video camera allows to visualize the crystal to optically align it in the X - ray beam and to measure the crystal dimensions and index crystal faces.

(2). Radiation safety enclosure with interlocks and warning lights

A common component of all systems in the D8 family is the radiation safety enclosure. The design is loaded to protect from stray radiation. The enclosure also includes warning lamps that alert you when X - ray are being generated.

(3). D8 controller

The D8 controller is an electronic module enclosed in the rack behind the front panel of the instrument. It contains all of the electronics and firmware for driving goniometer angles, opening the X - ray shutters, and monitoring other instrument functions such as safety interlocks, generator status, and detector status.

(4). Refrigerated recirculator for SMART PEX detector

The refrigerated recirculator uses Peltier technology to cool the CCD chip to a required -40°C to minimize dark currents.

(5). Computer

A high - speed computer which is used for control of the experiment storage of raw frame data, integration of data including solution and refinement of the structure. The computer uses the Microsoft Windows NT[®] operating system and including the software such as :

SMART program

This on - line program controls the instrument to collect the experimental data used by the other programs in the system program suite.

SMART off - line program

This off - line version performs many data display and manipulation functions but cannot control the instrument.

VIDEO program

This program controls the real - time video images from the video camera.

SAINT + program

This program sets up and carries out the integration process.

SHELXTL programs

This program suite produces a crystal structure from the integrated data.

2.7.4 Structure determination and refinement

2.7.4.1 Structure determination and refinement by SHELXTL program
version 6.12

The integration process, SAINT, has produced two important files there are name.p4p which contain the final unit cell parameters and other important information on how the experiment was carried out and name.raw which contain the actual intensity data. These files are all that is required to begin the structure solution and refinement process. The various steps in solving and refining the structure are carried out using the programs of the SHELXTL package. A simplified flow chart is shown in Figure 45.

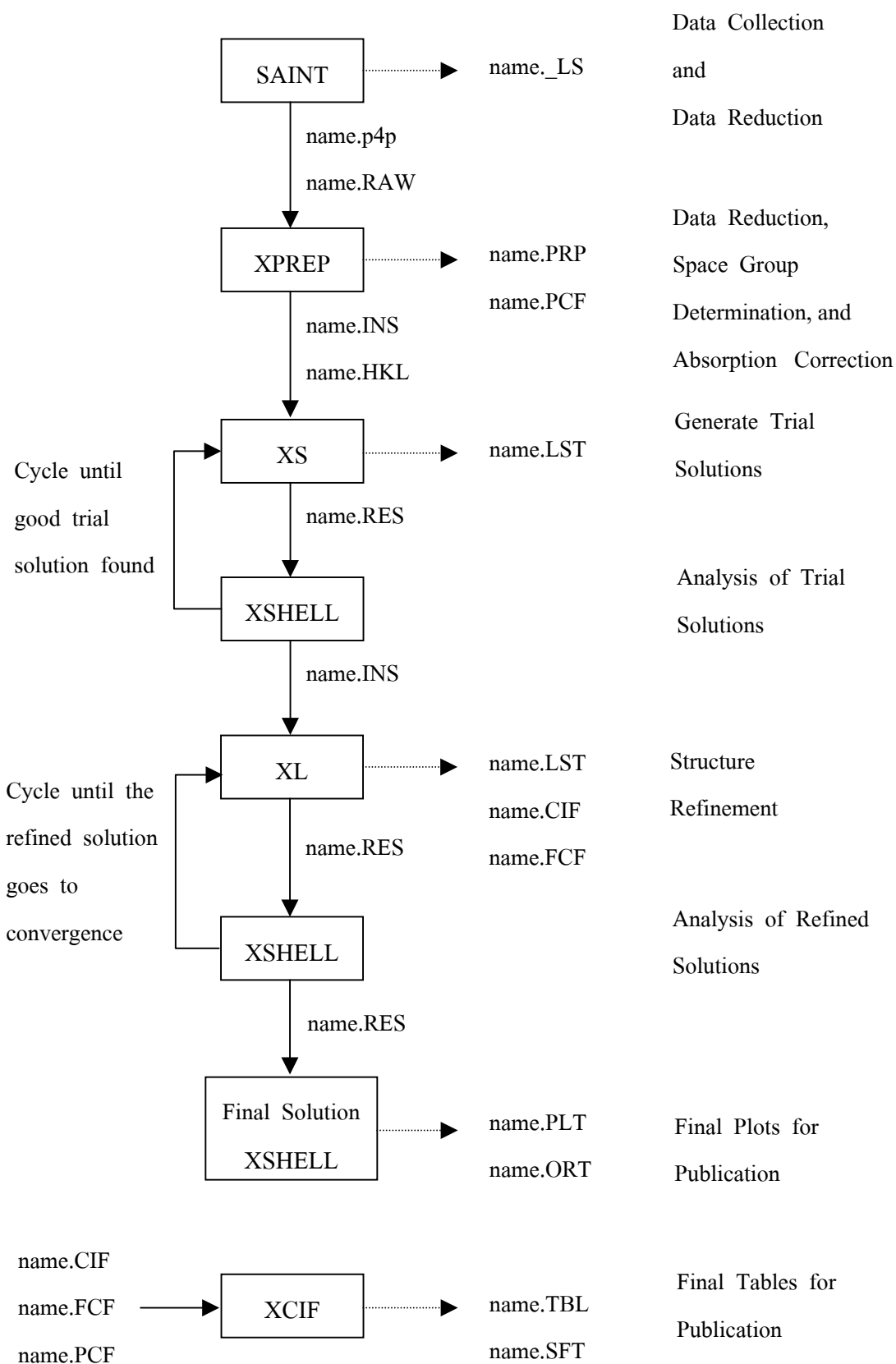


Figure 45. Flow chart of structure determination and refinement.

2.7.4.2 Structure determination and refinement by Xtal program version 3.6

The structure of $[\text{Cu}(\text{etu})_3]_2\text{SO}_4$ and $[\text{Cu}_2(\text{detu})_6](\text{NO}_3)_2$ were solved from diffraction data by using program Xtal 3.6 (Hall, et al. 1999) on PC computer. The Xtal calculations are initiated and controlled from input file known as name.dat file. The results of calculation are output to files and screen device as in graphics application. Xtal calculations use various files to store intermediate and archival data.

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 "compid". This is the method step by step of solving :

(1). Getting started

This step is making binary data files that are used extensively as working files and to archive certain types of data. The used subprograms are

STARTX : Create an Xtal binary data file

ADDREF : Add reflection data to the bdf

SORTRF : Sort and average reflection data

(2). Solving the structure

There are two methods that were to solve the structures :

(a). Heavy atom methods

The methods involve solving structure of compounds that have heavy atoms. The used subprograms are

GENEV : Normalize structure factors

FOURR : Reciprocal to real fourier transform

PEKPIK : Electron density maxima search

(b). Direct methods

The methods involve solving structure of compounds that have not heavy atoms.

(3). Refining the structure

In order to know the atomic positions more precisely so that better values of bond lengths and bond angles will be available. The process of obtaining atomic parameters that are more precise than those obtained from an initial model referred to as refinement of the crystal structure which is an essential part of any crystal structure analysis. The positions x , y , and z and the atomic displacement parameters, B , derived for each atom in a preliminary crystal structure are adjusted so as to improve the agreement between the observed structure amplitudes, $|F(hkl)|_O$ and those calculated from the determined model $|F(hkl)|_C$. The progress in improving this agreement is usually monitored by a residual index known as the R value, defined as :

$$R = \frac{\sum_{\text{all hkl}} \left| |F(hkl)|_O - |F(hkl)|_C \right|}{\sum_{\text{all hkl}} |F(hkl)|_O}$$

The R value is calculated as a measure of the precision of the result of the refinement. Therefore, if the R value is this high, the derive structure is not likely to be correct. Much lower R values are needed. The used subprograms are :

ADDATM : Add atom parameters

CRYLSQ : Crystallographic least - squares refinement

BONDLA : Bond lengths and angles

(4). Preparation for publication

This step is showing the result by pictures and numerical parameters for report and publishing. The used programs are :

LSQPL : Calculate least - squares planes
ORTEP : Oak ridge thermal ellipsoid plot
PLOTX : Soft interface to plotting devices
ATABLE : Tabulate atomic parameters
LISTEC : List reflection data in compact format
CIFIO : Archive and CIF input output