

## Chapter 2

### Methods

#### 2.1 Chemicals

##### 2.1.1 Materials from Ajax, Australia

Potassium oxalate ( $(\text{COOK})_2 \cdot \text{H}_2\text{O}$ ), Code no. AF401429, A.R. grade

Aluminium sulfate ( $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ ), Code no. F3D316, A.R. grade

##### 2.1.2 Materials from Lab-scan, Thailand

Sodium hydroxide ( $\text{NaOH}$ ), Code no. K2001, A.R. grade

##### 2.1.3 Materials from Merck, Germany

Oxalic acid dihydrate ( $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ ), Code no. 925A427292, A.R. grade

Sodium chloride ( $\text{NaCl}$ ), Code no. 923K12377304, A.R. grade

Methanol ( $\text{CH}_3\text{OH}$ ), Code no. 1.06009.2500, A.R. grade

Hydrochloric acid fuming 37% ( $\text{HCl}$ ), Code no. 1.00317.2500, A.R. grade

##### 2.1.4 Materials from J.T.Baker, U.S.A.

Potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ), Code no. 1-3094, A.R. grade

Sulfuric acid ( $\text{H}_2\text{SO}_4$ ), Code no. 9681-03, A.R. grade

##### 2.1.5 Materials from BDH, England

Potassium permanganate ( $\text{KMnO}_4$ ), Code no. 29644, A.R. grade

Samarium oxide ( $\text{Sm}_2\text{O}_3$ ), Code no. 30040, A.R. grade

Neodymium oxide ( $\text{Nd}_2\text{O}_3$ ), Code no. 29306, A.R. grade

Dysprosium oxide ( $\text{Dy}_2\text{O}_3$ ), Code no. 28283, A.R. grade

Gadolinium oxide ( $\text{Gd}_2\text{O}_3$ ), Code no. 28442, A.R. grade

Praseodymium oxide ( $\text{Pr}_6\text{O}_{11}$ ), Code no. 29670, A.R. grade

##### 2.1.6 Material from Hopkin&Williams Ltd, England

Yttrium oxide ( $\text{Y}_2\text{O}_3$ ), Laboratory reagent

## 2.2 Instruments

### 2.2.1 Department of Chemistry, PSU

1. UV-Visible spectrophotometer, SPECORD S100, Analytik Jena GmbH, Germany.
2. UV-Visible spectrophotometer, UV-2401, Shimadzu, Japan.
3. Single crystal X-ray diffractometer; SMART APEX CCD, Bruker, Germany.

### 2.2.2 Scientific Equipment Center, PSU

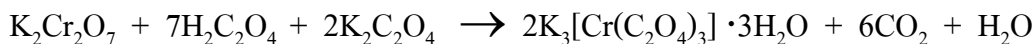
1. Electron Probe Microanalyzer, JXA-8800R, JEOL, Japan, and Energy Dispersive X-ray Spectrometer, EDX:Oxford ISIS 300, England.
2. Fourier-Transformed NMR spectrometer 500MHz, Model UNITY INOVA, Varian, Germany.
3. X-ray fluorescence spectrometer, PHILIPS PW 2400, The Netherlands.
4. X-ray diffractometer, XRD; PHILIPS X'Pert MPD, The Netherlands.

### 2.2.3 Central Equipment Unit, Faculty of Science, PSU

1. Inductively-coupled plasma/atomic emission spectrometer, ICP-AES; Optima4300DV, Perkin Elmer, USA.

## 2.3 Preparation of oxalato complexes

### 2.3.1 Synthesis of $K_3[Cr(C_2O_4)_3] \cdot 3H_2O$ complex (Booth, 1939)



To a solution of 23 g of potassium oxalate monohydrate and 55 g of oxalic acid dihydrate in 800 ml. of water was added 19 g of powdered potassium dichromate in small portions with vigorous stirring. When the reaction ended, the solution was evaporated nearly to dryness and allowed to crystallize. Potassium trioxalatochromate formed as deep-green crystals with a brilliant blue iridescence. Yield 45 g (90 percent).

### 2.3.2 Synthesis of $K_3[Al(C_2O_4)_3] \cdot 3H_2O$ complex (Booth, 1939)



A solution of 67 g (0.1 mol) of aluminium sulfate,  $Al_2(SO_4)_3 \cdot 18H_2O$ , was treated with a solution of 24 g of sodium hydroxide. The precipitated aluminium hydroxide was filtered, washed, and boiled with a solution of a mixture of 55.2 g of potassium oxalate monohydrate and 37.8 g of oxalic acid dihydrate. After boiling material which did not dissolve was filtered out and the filtrate was evaporated to crystallization. The yield was nearly quantitative.

### 2.3.3 Synthesis of the RedCubic, RedHexagonal and Blue crystals

(Laongjit, 2004)

The aqueous solutions of  $K_3[Cr(C_2O_4)_3] \cdot 3H_2O$  (0.2437 g, 0.5 mmol) and  $K_3[Al(C_2O_4)_3] \cdot 3H_2O$  (4.3889 g, 9.49 mmol) were mixed and aqueous solution of NaCl (1.1688 g, 0.02 mol) was added. The solution was evaporated to small volume. The blue crystals appeared after one week. The crystals were filtered out and successively washed with a mixture of water-methanol(1:1). Red crystals appeared after one week in the filtrate. Three types of crystals were obtained two with dark red color almost black and the other was blue color. The two red crystals were named as RedCubic and RedHexagonal to reflect the physical appearance of crystals and likewise for the Blue.

### 2.3.4 Synthesis of the AlCubic

The aqueous solutions of  $K_3[Al(C_2O_4)_3] \cdot 3H_2O$  (4.3889 g, 9.49 mmol) and excess NaCl (1.688 g) were mixed. The solution was evaporated to small volume. Only AlCubic crystals appeared after one week. The crystals were filtered out and successively washed with a mixture of water-methanol(1:1).

### 2.3.5 Synthesis of the RedCubic by varying %Cr

The aqueous solutions of  $K_3[Cr(C_2O_4)_3] \cdot 3H_2O$  (x mmol) and  $K_3[Al(C_2O_4)_3] \cdot 3H_2O$  (1-x mmol) were mixed and aqueous solution of NaCl (1.688g ) was added. The solution was evaporated to small volume. Only Redcubic crystals appeared after one week. The crystals were filtered out and successively washed with a mixture of water-methanol(1:1).

### 2.3.4 Synthesis of the Blue by varying %Cr

The Blue crystal was prepared by mixing aqueous solutions of  $K_3[Cr(C_2O_4)_3] \cdot 3H_2O$  (x mmol) and  $K_3[Al(C_2O_4)_3] \cdot 3H_2O$  (1-x mmol) and the solution of  $Pr_6O_{11}$  was added. The solution was evaporated to small volume. Only Blue crystals appeared after one week. The crystals were filtered out and successively washed with a mixture of water-methanol(1:1).

## 2.4 Products characterizations

### 2.4.1 UV-Visible absorption spectrometry (UV-Vis)

Normally, samples for UV-Vis spectrophotometry were investigated in solution form, however, when applicable other forms, such as crystalline and powder, were also used.

Solution samples were placed in matched set of glass 10 mm square spectrophotometer quartz cells (Figure 5(a)). Ultraviolet-Visible spectra were recorded with SPECORD S100 spectrophotometer. The absorption spectra in water solution were monitored in the 200-800 nm range.

Crystalline solid samples were placed in cells(Figure 5(b)). Ultraviolet-Visible spectra were recorded with SPECORD S100 spectrophotometer. The absorption spectra of solid sample were monitored in the 200-800 nm range.

Powder samples were placed in matched set of the dish(Figure 5(c)). Ultraviolet-Visible spectra were recorded with Shimadzu UV-2401 spectrophotometer and monitored in the range the 240-800 nm.

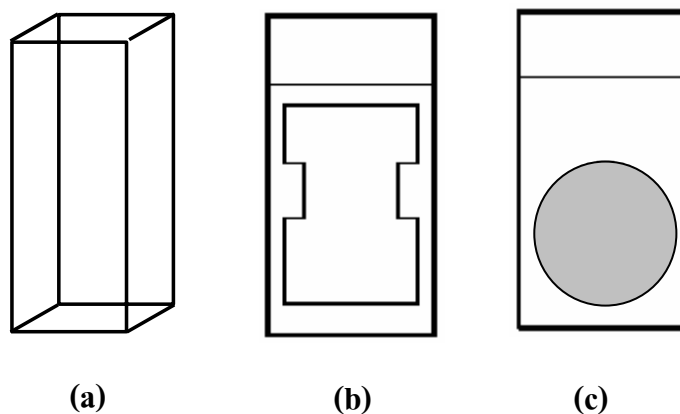


Figure 5 (a) cell for solution sample, (b) cell for crystalline solid sample, and (c) cell for powder

#### 2.4.2 $^{13}\text{C}$ -NMR spectroscopy

Samples were dissolved in  $\text{D}_2\text{O}$ .  $^{13}\text{C}$  chemical shift was referred to the central peak of  $\text{DMSO-}d_6$  (39.7 ppm). Spectra were recorded with Fourier-Transformed NMR spectrometer 500 MHz, Model UNITY INOVA, Varian, Germany.

#### 2.4.3 X-ray powder diffraction patterns (XRD)

The XRD spectra were obtained through the Scientific Equipment Center, Prince of Songkla University, Hat Yai, Songkla, using an x-ray diffractometer,  $\text{Cu K}\alpha$  radiation, X'Pert MPD Philips.

#### 2.4.4 Single crystal X-ray crystallography

Crystal diffraction data were recorded with SMART APEX CCD X-ray diffractometer. In addition, the Xtal program was used to study the crystal structures with population method.

#### 2.4.5 Electron probe microanalyzer / energy dispersive X-ray fluorescence (EPMA/EDX)

The elemental composition was checked by EPMA/EDX. The energy dispersive X-ray fluorescence (EDXRF) spectrometer (Oxford ISIS 300) is of the tube type. The excitation X-ray is generated from a tube using a Rh target.

#### 2.4.6 Wavelength dispersive X-ray fluorescence spectrometer(WDXRF)

The pressed powder samples were detected with wavelength dispersive X-ray fluorescence(WDXRF) spectrometer, PW2400, Philips Analytical X-ray B.V., The Netherlands. The X-ray tube uses Rh as target.

#### 2.4.7 Crystal density measurement

Density of the single crystal samples were measured by the floating technique. In this technique, one must prepare a solution that has the same density as that of the single crystal sample (the crystal can float in the middle of this solution). The density of this solution is then measured and taken as the density of the crystal.

The steps for the measurement of density of the solution are as follows.

1. Determine the volume of the pycnometer
  - Take a dry and clean 5 mL pycnometer, measure its full weight (including the stopper) on an analytical scale ( $m_1$ ). Note the room temperature.
  - Fill the pycnometer with room temperature distilled water. Make sure there are no bubbles under the water level. Fill up a little higher than the mark on the pycnometer.

- Dry the outside of the pycnometer using a dry cloth. Make sure to hold the pycnometer only at the bottleneck as your hand might warm up the bottle ruining the calibration altogether.
- Remove the excess water (above the mark) from the pycnometer using a strip of filtering paper. Make sure there are no droplets above the mark.
- Determine the weight of the pycnometer plus the water ( $m_2$ ). Mind the thermometer again.
- The volume of the pycnometer can easily be obtained knowing the density of the water ( $\rho_v$ ) at the particular room temperature:

$$V = (m_2 - m_1) / \rho_v$$

## 2. Determination of the mass of the unknown solution

- Rinse the inside of the empty but still wet pycnometer with a small amount of the unknown liquid. Repeat three times. Fill it up, dry it, check for bubbles and droplets, then measure the weight on the analytical scale ( $m_3$ ).
- The mass of the solution:  $m_3 - m_1$

## 3. The ratio of the mass and the volume of the solution gives the density:

$$\rho = \rho_v (m_3 - m_1) / (m_2 - m_1)$$

#### 2.4.8 Inductively-coupled plasma/atomic emission spectroscopy (ICP-AES)

To determine the elemental composition of complexes the ICP-AE spectrometer (Perkin Elmer, Optima 4300DV, USA.) was used and the data were acquired at the Central Equipment Unit, Prince of Songkla University.