

2. Methods of study

2.1 Chemicals

2.1.1 Materials from Fluka AG, Switzerland

Potassium oxalate monohydrate, $(\text{COOK})_2\text{H}_2\text{O}$, Code no.60425, A.R grade

Aluminium sulfate, $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$, Code no. 06421, A.R grade

Polyethylene powder, Code no. 81149, A.R.grade

2.1.2 Materials from Carlo Erba

Oxalic acid dihydrate, $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$, Code no. 408736, A.R grade

Sodium oxalate, $(\text{COONa})_2$, Code no. 482065, A.R grade

2.1.3 Materials from Merck

Sodium hydroxide, NaOH , Code no. 1.06498.1000, A.R grade

Sodium chloride, NaCl , Code no. 6404, A.R grade

Methanol, CH_3OH , Code no. 1.06009.2500, A.R grade

Ethanol, $\text{C}_2\text{H}_5\text{OH}$, Code no. 1.00983.2500, A.R grade

Acetone, $\text{C}_2\text{H}_6\text{O}$, Code no. 1.00014.2500, A.R grade

2.1.4 Materials from J.T.Baker

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

Sulfuric acid, H_2SO_4 , Code no. 9681-03, A.R grade

2.1.5 Materials from Mallinckrodt, inc

Potassium bromide, KBr , Code no. 0505, A.R grade

2.1.6 Material from BDH

Silver nitrate, AgNO_3 , A.R grade

2.2 Instruments

2.2.1 Chemistry Department, PSU

1. UV-Visible spectrophotometer; SPECORD S100, Analytik Jena GmbH, Germany.
2. Fourier-transformed infrared spectrophotometer, FT-IR; GX FT-IR, Perkin Elmer, England.
3. Single crystal x-ray diffractometer; SMART APEX CCD, Bruker, Germany.

2.2.2 Scientific Equipment Center, PSU

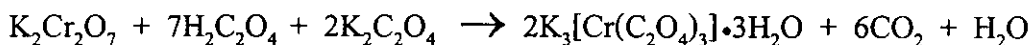
1. Thermogravimetry analyzer; TGA7, Perkin Elmer, Singapore.
2. Differential scanning calorimeter, DSC; DSC7, Perkin Elmer, Singapore.
3. Scanning electron microanalyzer/Energy dispersive x-ray fluorescence spectrometer, SEM/EDX; SEM: JSM-5800LV, JEOL, Japan and EDX: Oxford ISIS 300, Oxford Instruments (UK) Ltd., England.
4. Elemental analyzer, CE Flash 1112 Series EA, Thermoquest, Italy.

2.2.3 Central Equipment Unit, Faculty of Science, PSU

1. X-ray diffractometer, XRD; PW 3710 mpd control, Philips, Holland.
2. Inductively coupled plasma atomic emission spectroscopy, ICP-AES; Optima 4300DV, Perkin Elmer, USA.

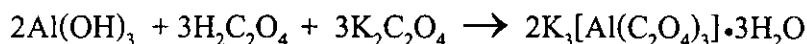
2.3 Preparation of oxalato complexes

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, RedRhombic and Blue crystals

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.

2.4 Products characterizations

2.4.1 Titration technique

Determination of the percentage of oxalate group was carried out by titration. Dissolved a weighed sample (0.2 g) in about 50 ml. of dilute sulphuric acid in a 250 mL conical flask, heated the solution on a hotplate to the boiling temperature, and titrated it with a solution of potassium permanganate (about decinormal) which had been standardized with sodium oxalate and noted the volume of the KMnO_4 solution. For the latter purpose treated 0.15 g of pure salt in the same way as the complex salts. Calculated the theoretical value of the percentage of oxalate in the complexes.

2.4.2 UV-Visible absorption spectrometry (UV-Vis)

Ultraviolet-Visible spectra were recorded with SPECORD S100 spectrophotometer. The absorption spectra in water solution were monitored in the 200-800 nm range. Solution samples were placed in matched set of glass 10 mm square spectrophotometer cells. The solid state were recorded with UV-2401 spectrophotometer and monitored on the 240-800 nm.

2.4.3 Infrared spectrometry (IR)

All infrared spectra were recorded with Perkin Elmer Spectrum GX FTIR-spectrophotometer with accuracy $\pm 2 \text{ cm}^{-1}$ (calibrated against polystyrene) and monitored in the 4000-370 cm^{-1} range. Solid samples were examined as KBr pellets.

2.4.4 X-ray powder diffraction patterns (XRD)

The XRD spectra were obtained through the Equipment Division of the Faculty of Science, Prince of Songkla University, Hat Yai, Songkla using an x-ray diffractometer, PW 3710 mpd control, Ni filtered $\text{Cu K}\alpha$ radiation, Philips.

2.4.5 Single crystal x-ray crystallography

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

2.4.6 Scanning electron microscope/Energy dispersive x-ray fluorescence (SEM/EDX)

The element composition was checked by SEM/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. The detector is Si (Li) with resolution of 164 eV for the Mn K α line.

2.4.7 Thermogravimetric analysis (TGA)

Mass change with temperature was studied in the range 50-1200 $^{\circ}$ C under air atmosphere with heating rate of 10 $^{\circ}$ C per minute (TGA7, Perkin Elmer, U.S.A.). All data were acquired by the Scientific Equipment Center, Prince of Songkla University, Hat Yai, Songkla.

2.4.8 Differential scanning calorimetric (DSC)

The change of energy with temperature was studied in the temperature range 50-500 $^{\circ}$ C under air atmosphere with heating rate of 10 $^{\circ}$ C per minute (DSC7, Perkin Elmer, U.S.A.). All data were acquired by the Scientific Equipment Center, Prince of Songkla University, Hat Yai, Songkla.

2.4.9 Inductively coupled plasma atomic emission spectroscopy (ICP-AES)

Samples were checked with Perkin Elmer, Optima 4300DV, USA. All data were acquired by the Central Equipment Unit, Prince of Songkla University, Hat Yai, Songkla.

2.4.10 Elemental analysis (CHNS-O)

The composition of C, H, and O atom in complexes were determined at the Scientific Equipment Center, Prince of Songkla University, Hat Yai, Songkla by the CE Flash 1112 Series EA CHNS-O Analyzer.