

CHAPTER 3

EXPERIMENTAL

3.1 Materials

The sources of the materials used, without further purification, in this study are given below:

CoCO₃ (BDH)

CoCl₂.6H₂O (Riedel de Haen)

NaOH (Glassworld)

99% Glacial acetic acid (ACE)

99% Propionic acid (Aldrich)

99+% Butyric acid (Aldrich)

99% Valeric acid (Aldrich)

99% Hexanoic acid (Aldrich)

99% Heptanoic acid (Aldrich)

99.5+% Octanoic acid (Aldrich)

96% Nonanoic acid (Aldrich)

99-100% Decanoic acid (Sigma)

Hexane distilled from sodium

Distilled AR grade acetone

Distilled water

3.2 Synthetic Methods

Experiment 1a: Synthesis of cobalt acetate using CoCO_3 ^{1,2}

CoCO_3 (11.895 g, 0.100 mol) was dissolved in 50 ml hot distilled water (60 °C). $\text{CH}_3\text{CO}_2\text{H}$ (12.073 ml) was added dropwise to the carbonate solution, whereafter the reaction temperature was increased to 100 °C. Heating was continued until the volume of solvent was reduced to ~ 20 ml. The solution was cooled to room temperature and allowed to stand for 24 hours during which time a sticky solid formed. The supernatant liquid was decanted off and the solid dissolved in ~ 20 ml of hot distilled water. The solution was filtered whilst still warm. After several days, needle-like maroon crystals formed which were collected and dried at 90 °C for 2 hours. Upon drying, the crystals became violet in colour and powdery in texture. The final yield was determined to be 12%. The product was characterized using TG, DSC and IR techniques.

Experiment 1b: Synthesis of cobalt acetate using $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$

$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (1.002 g, 0.00421 mol) was dissolved in 20 ml glacial acetic acid. The solution was refluxed at 120 °C for 2-3 hours. Upon cooling, a fine pink-red precipitate formed which was collected by filtration on a Hirsch funnel. The solid was washed with cold, distilled water and dried at 90 °C for 2 hours. The solid changed to a deep purple colour. The product was characterized using IR spectroscopy. The yield was determined to be 55%.

Experiment 2a: Synthesis of cobalt propionate using CoCO_3 ³

CoCO_3 (11.894 g, 0.100 mol) was dissolved in 50 ml hot distilled water (60 °C). $\text{C}_2\text{H}_5\text{CO}_2\text{H}$ (14.965 ml) was added dropwise to the carbonate solution, whereafter the reaction temperature was increased to 100 °C. Heating was continued until the volume of solvent was reduced to ~ 20 ml. The solution was cooled to room temperature and allowed to stand for 24 hours during which time a sticky solid

formed. The supernatant liquid was decanted off and the solid dissolved in ~ 20 ml of hot distilled water. The solution was filtered whilst still warm. After several days, block-like maroon crystals formed. A few of these crystals were selected for single crystal XRD analysis and the remainder was dried at 90 °C for 2 hours. Upon drying, the crystals became violet in colour and powdery in texture. The final yield was determined to be 15%. The product was characterized using TG, DSC and IR techniques.

Experiment 2b: Synthesis of cobalt propionate using $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$

$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (1.003 g, 0.00422 mol) was dissolved in 20 ml propionic acid and the solution was refluxed at 140 °C for 1-2 hours. After a period of cooling, a fine pink precipitate settled out which was collected by filtration on a Hirsch funnel and washed with cold, distilled water. After drying at 90 °C for 2 hours, the solid became dark purple and flaky. The yield was determined to be 63%. The product was characterized using IR techniques.

Experiment 3: Synthesis of cobalt butyrate using CoCO_3

CoCO_3 (11.895 g, 0.100 mol) was dissolved in 50 ml hot distilled water (60 °C). $\text{C}_3\text{H}_7\text{CO}_2\text{H}$ (17.805 ml) was added dropwise to the carbonate solution, whereafter the reaction temperature was increased to 100 °C. Heating was continued until the volume of solvent was reduced to ~ 20 ml. The solution was cooled to room temperature and allowed to stand for 24 hours during which time a sticky solid formed. The supernatant liquid was decanted off and the solid was dissolved in ~ 20 ml of hot distilled water. The solution was filtered whilst still warm. After several days, fine ruby-red crystals formed which were collected and dried at 90 °C for 2 hours. Upon drying, the crystals became violet in colour and powdery in texture. The final yield was determined to be 23%. The product was characterized using TG, DSC and IR techniques.

Experiment 4: Synthesis of cobalt valerate using CoCO_3

CoCO_3 (11.895 g, 0.100 mol) was dissolved in 50 ml hot distilled water (60 °C). $\text{C}_4\text{H}_9\text{CO}_2\text{H}$ (20.632 ml) was added dropwise to the carbonate solution, whereafter the reaction temperature was increased to 100 °C. Heating was continued until the volume of solvent was reduced to ~ 20 ml. The solution was cooled to room temperature and allowed to stand for 24 hours during which time a sticky solid formed. The supernatant liquid was decanted off and the solid was dissolved in ~ 20 ml of hot distilled water and the solution filtered whilst still warm. After several days, no solid formed and the solution was evaporated to dryness. The maroon solid was washed with ice cold distilled water and dried at 90 °C for 2 hours. Upon drying, the solid became violet in colour and powdery in texture. The final yield was determined to be 11%. The product was characterized using TG, DSC and IR techniques.

Experiment 5a: Synthesis of cobalt hexanoate using CoCO_3

CoCO_3 (11.891 g, 0.100 mol) was dissolved in 50 ml hot distilled water (60 °C). $\text{C}_5\text{H}_{11}\text{CO}_2\text{H}$ (23.467 ml) was added dropwise to the carbonate solution, whereafter the reaction temperature was increased to 100 °C. Heating was continued until the volume of solvent was reduced to ~ 20 ml. The solution was cooled to room temperature and allowed to stand for 24 hours but no solid formed during this time. The solution was evaporated to dryness and the resulting solid was dissolved in ~ 20 ml hot distilled water and the solution filtered whilst still hot. After several days, violet solid precipitated out which was collected and dried at 90 °C for 2 hours. The final yield was determined to be 8%. The product was characterized using TG, DSC and IR techniques.

Experiment 5b: Synthesis of cobalt hexanoate using $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$

$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (2.036 g, 0.00856 mol) was dissolved in 100 ml distilled water and 20 ml of propionic acid was added to this solution. The acid was only partially soluble in the water. Consequently, the solution was heated and stirred vigorously for a number of hours to ensure thorough enough mixing for a reaction to occur. After some hours, a sticky maroon solid formed. The remaining solvent mixture was decanted off and the solid washed thoroughly with cold hexane. Upon drying at 90 °C for 2 hours, the solid became violet and flaky. The final yield was determined to be 48%. The product was characterized using IR techniques.

Experiment 6a: Synthesis of cobalt heptanoate using CoCO_3

CoCO_3 (11.894 g, 0.100 mol) was dissolved in 50 ml hot distilled water (60 °C). $\text{C}_6\text{H}_{13}\text{CO}_2\text{H}$ (26.301 ml) was added dropwise to the carbonate solution, whereafter the reaction temperature was increased to 100 °C. Heating was continued until the volume of solvent was reduced to ~ 20 ml. The solution was cooled to room temperature and allowed to stand for 24 hours during which time an amorphous violet solid formed. The solid was collected and washed with cold, distilled hexane and dried at 90 °C for 2 hours. The final yield was determined to be 35%. The product was characterized using TG, DSC and IR techniques.

Experiment 6b: Synthesis of cobalt heptanoate using $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$

$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (1.512 g, 0.00635 mol) and 20 ml heptanoic acid were dissolved in 40 ml distilled AR grade acetone. The solution was refluxed at 60 °C for ~ 1 hour. The solvent was reduced to half its original volume and the solution cooled for a number of hours. A fine amorphous pink solid precipitated out which was collected by filtration on a Hirsch funnel and washed with cold hexane. After drying at 90 °C for 2 hours, the solid became violet. The final yield was determined to be 40%. The product was characterized using IR techniques.

Experiment 7a: Synthesis of cobalt octanoate using CoCO_3

CoCO_3 (11.892 g, 0.100 mol) was dissolved in 50 ml distilled hexane (60 °C). $\text{C}_7\text{H}_{15}\text{CO}_2\text{H}$ (28.989 ml) was added dropwise to the carbonate solution. Heating was continued until the volume of solvent was reduced to ~ 20 ml. The solution was cooled to room temperature and allowed to stand for 24 hours whereafter no solid formed. The solution was heated until all the solvent was removed and the resulting flaky violet solid was washed several times with cold, distilled hexane and then dried at 90 °C for 2 hours. The final yield was determined to be 18%. The product was characterized using TG, DSC and IR techniques.

Experiment 7b: Synthesis of cobalt octanoate using $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$

$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (1.516 g, 0.00637 mol) and 20 ml octanoic acid were dissolved in 40 ml distilled AR grade acetone. The solution was refluxed at 60 °C for ~ 1 hour. Heating was continued until the solvent was reduced to half its original volume and the solution was then cooled for a number of hours. A maroon amorphous solid precipitated out which was collected by filtration on a Hirsch funnel and washed with cold hexane. After drying at 90 °C for 2 hours, the solid turned violet. The final yield was determined to be 44%. The product was characterized using IR techniques.

Experiment 8a: Synthesis of cobalt nonanoate using CoCO_3

CoCO_3 (11.893 g, 0.100 mol) was dissolved in 50 ml distilled hexane (60 °C). $\text{C}_8\text{H}_{17}\text{CO}_2\text{H}$ (31.968 ml) was added dropwise to the carbonate solution, whereafter the volume of solvent was reduced to ~ 20 ml. The solution was cooled to room temperature and allowed to stand for 24 hours. An oily solid formed and the solution was heated further to remove all the solvent. The resulting violet wax-like solid was washed several times with cold, distilled hexane and then dried at

90 °C for 2 hours. The final yield was determined to be 40%. The product was characterized using IR techniques.

Experiment 8b: Synthesis of cobalt nonanoate using $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$

NaOH (0.301 g, 0.0063 mol) were dissolved in 20 ml distilled water. Nonanoic acid (1.068 g, 0.0063 mol) was added to the NaOH solution and the solution was refluxed at 140 °C for ~ 8 hours. After cooling for 1 hour, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.808 g, 0.0032 mol) was added to the solution and heated gently for ~ 4 hours. A violet product precipitated out of solution. The product was filtered out and washed several times with warm distilled water. After drying at 80°C for 2 hours, the final yield was determined to be 71%. The product was characterized using TG, DSC and IR techniques.

Experiment 9: Synthesis of cobalt decanoate using $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$

NaOH (0.232 g, 0.0058 mol) was dissolved in 20 ml distilled water. Decanoic acid (1.027 g, 0.0058 mol) was added to the NaOH solution and the solution was refluxed at 140 °C for ~ 8 hours. After cooling for 1 hour, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.794 g, 0.0029 mol) was added to the solution and heated gently for ~ 2 hours. A violet product precipitated out of solution. The product was filtered out and washed several times with warm distilled water. After drying at 80°C for 2 hours, the final yield was determined to be 62%. The product was characterized using TG, DSC and IR techniques.

3.3 Characterization Methods

- **Elemental analysis**

Carbon and hydrogen contents of the products were determined using standard combustion techniques (ISCW).

- **Infrared spectroscopy**

All infrared spectra of the products were recorded on a Bruker Vector 22 instrument as KBr pellets over the transmittance range 550-4000 cm^{-1} at a spectral resolution of 4 cm^{-1} . Samples were gently ground to a homogenous powder. Data resolution was done with Microsoft Excel.

- **Thermal analysis**

Thermal analysis measurements (TGA, DTG and DSC) were carried out on a TA instruments SDT 2960 simultaneous thermal analyzer. Experiments were performed in a dynamic atmosphere (flow rate ~ 100 ml/min) of dry argon over the range 25 – 500°C. To avoid variations in thermal responses caused by mass effects, constant masses of 15 – 20 mg of powdered sample were used for each analysis. All analyses were repeated in duplicate to ensure consistency of data and mass losses reported are an average of duplicate measurement. Heating rates of 10°C/min were used unless otherwise specified. Temperature calibrations on the instrument were carried out using pure indium and zinc metals: melting points 156.6 and 419.5°C respectively. Heat flow calibrations were done using TA instruments sapphire standard. Data resolution was done with TA universal analysis software.

- **Kinetic studies**

Cobalt propionate and cobalt decanoate (sample sizes ~20 mg per sequence) were heated at various rates: 2, 5, 10, 15 and 20°C/min in a dynamic flow of argon (flow rate ~100 ml/min) from 25 – 500°C. Data resolution was done with TA universal analysis. Activation energies, E_a , for the decarboxylation reactions of these samples were determined using the Kissinger method.

- **Mass spectrometry**

Mass spectral data was recorded on a Pfeiffer Quadropole mass spectrometer equipped with a Channeltron detector. Cycles were recorded every 60 seconds. Data resolution was done with Microsoft Excel.

3.4 References

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- ³ P. S. Bassi, H. S. Jamwal and B. S. Randhawa, *Thermochim. Acta*, **71** (1983) 15
- ⁴ *Encyclopedia of chemical technology Vol. 8*, Wiley & Sons, New York, 1991, p.435