CHAPTER 3 EXPERIMENTAL

This research is focussed on the development of the synthetic methods and characterisation of two types of ionic copper(II) mixed carboxylates of general formula: (a) $K_a[Cu_2(p\text{-}OC_6H_4COO)_a(CH_3(CH_2)_nCOO)_{4-a}]$, and (b) $[Cu_2(p\text{-}H_3NC_6H_4COO)_a(CH_3(CH_2)_nCOO)_{4-a}]X_a$, where $a = 1, 2$; $n = 14, 10, 8$ and 6; X = Cl, CH_3COO and CF_3SO_3.

The chemicals used were listed in **Table 3.1.** These chemicals were commercially available and used as received.

Table 3.1 Chemicals used in the project

NAME	FORMULA	FORMULA WEIGHT (g/mol)
Propanoic acid	CH_3CH_2COOH	74.08
Butanoic acid	$CH_3(CH_2)_2COOH$	88.11
Pentanoic acid	$CH_3(CH_2)_3COOH$	102.13
Hexanoic acid	$CH_3(CH_2)_4COOH$	116.16
Octanoic acid	$CH_3(CH_2)_6COOH$	144.21
Decanoic acid	$CH_3(CH_2)_8COOH$	172.26
Dodecanoic acid	$CH_3(CH_2)_{10}COOH$	200.32
Hexadecanoic acid	$CH_3(CH_2)_{14}COOH$	256.41
p-Aminobenzoic acid	$p\text{-}H_2NC_6H_4COOH$	137.14
p-Hydroxybenzoic acid	$p\text{-}HOC_6H_4COOH$	138.12
Copper(II) chloride dihydrate	$CuCl_2.2H_2O$	170.48
Copper(II) hydroxide carbonate	$CuCO_3.Cu(OH)_2$	221.20
Copper(II) acetate monohydrate	$Cu(CH_3COO)_2.H_2O$	199.65
Sodium carbonate	Na_2CO_3	105.98
Pyridine	C_5H_5N	79.1
3,3-dimethyl-2-butanone	$C_6H_{12}O$	100.16

3.1 METHOD DEVELOPMENT

The initial challenge in this project was to find the most suitable method to prepare the designed ionic copper(II) mixed carboxylates. Three methods were tried: (a) one-pot synthesis, (b) ligand-exchange reaction, and (c) carbonate-base-acid reaction. The complexes chosen were $K_2[Cu_2(p\text{-}OC_6H_4COO)_2(CH_3(CH_2)_{14}COO)_2]$ and $[Cu_2(p\text{-}H_3NC_6H_4COO)_2(CH_3(CH_2)_{14}COO)_2]Cl_2$.

3.1.1 $K_2[Cu_2(p\text{-}OC_6H_4COO)_2(CH_3(CH_2)_{14}COO)_2]$

(a) One-pot synthesis

$CH_3(CH_2)_{14}COOH$ (5.00 g, 19.5 mmol) and $p\text{-}HOC_6H_4COOH$ (2.69 g, 19.5 mmol) were added to an ethanolic solution of KOH (124.9 mmol; 100 ml). The mixture was heated until all solids dissolved. $CuCl_2.2H_2O$ (3.32 g, 19.5 mmol) was added to the above solution, forming a black powder immediately. The reaction mixture was magnetically stirred and gently heated for 30 minutes. The solid formed was filtered from the warm reaction mixture, washed with CH_3CH_2OH, followed by CH_3COCH_3, and dried in a warm oven (60^oC) to give a fine dark brown powder. The yield was 5.96 g (47.0%).

(b) Ligand-exchange reaction

The ligand-exchange reaction involved five steps.

Step 1. *Synthesis of* $CH_3(CH_2)_{14}COONa$

$CH_3(CH_2)_{14}COOH$ (24.68 g, 96.2 mmol) was added portionwise to an aqueous solution of Na_2CO_3 (5.10 g, 48.1 mmol). The cloudy mixture was gently heated and stirred on a hot plate for 30 minutes. It was then left to cool at room temperature, filtered and dried in a warm oven (60^oC) to give a white solid. The yield was 24.08 g (89.9 %).

***Step 2.** Synthesis of [$Cu_2(CH_3(CH_2)_{14}COO)_4$]*

$CH_3(CH_2)_{14}COONa$ (10.23 g; 36.7 mmol) was dissolved in CH_3CH_2OH (100 ml) by heating on a hot plate. $CuCl_2.2H_2O$ (3.12 g; 18.3 mmol) was added to the hot solution and the heating was continued for another 30 minutes. A greenish-blue fine powder formed was filtered under suction, washed with distilled water followed by CH_3CH_2OH, and dried in a warm oven (60^{o}C). The yield was 3.76 g (71.2 %).

***Step 3.** Synthesis of [$Cu_2(p\text{-}HOC_6H_4COO)_4$]*

p-HOC_6H_4COOH (6.90 g, 0.05 mol) was dissolved in CH_3CH_2OH (100 ml). The solution was magnetically stirred and gently heated on a hot plate. [$Cu(CH_3COO)_2$].H_2O (5.00 g, 0.025 mol) was added and heated for another 30 minutes. A fine peacock-blue powder slowly formed when the reaction mixture was left standing overnight at room temperature. It was filtered under suction and dried in a warm oven (60^{o}C). The yield was 7.26 g (70.8 %).

***Step 4.** Synthesis of [$Cu_2(p\text{-}HOC_6H_4COO)_2(CH_3(CH_2)_{14}COO)_2$]*

A mixture of [$Cu_2(CH_3(CH_2)_{14}COO)_4$] (0.50 g, 0.44 mmol) and [$Cu_2(p\text{-}HOC_6H_4COO)_4$] (0.29 g, 0.44 mmol) in CH_3CH_2OH (100 ml) was magnetically stirred and gently heated on a hot plate. C_5H_5N (~30 ml) was added dropwise to the hot mixture until a clear purplish blue solution formed. It was then further heated for an hour, and left at room temperature over night. The pale green fine powder formed was filtered, washed with CH_3CH_2OH, and dried in an oven at 80^{o}C for a week. The yield was 0.70 g (64.8 %).

***Step 5.** Ionisation of [$Cu_2(p\text{-}HOC_6H_4COO)_2(CH_3(CH_2)_{14}COO)_2$]*

[Cu_2(*p*-$HOC_6H_4COO)_2(CH_3(CH_2)_{14}COO)_2$] (0.15 g, 0.16 mmol) was dissolved in an ethanolic solution of KOH (0.32 mmol; 20 ml). The solution was stirred at room temperature for an hour, and the black fine powder formed was filtered, and dried in a warm oven. The yield was 0.09 g (56.2 %).

(c) Carbonate-base-acid reaction for the synthesis of [Cu_2(p-$HOC_6H_4COO)_2$ ($CH_3(CH_2)_{14}COO)_2$]

A mixture of $CH_3(CH_2)_{14}COOH$ (5.50 g, 21.4 mmol) and *p*-HOC_6H_4COOH (2.96 g, 21.4 mmol) was suspended in CH_3OH (150 ml). $CuCO_3.Cu(OH)_2$ (4.76 g, 21.4 mmol) was added, and the reaction mixture was magnetically stirred and heated at 60°C for one week to give a mixture of greenish blue slurry. C_5H_5N (30 ml) was added to the hot mixture, which was further heated at 60°C for one hour. It was then filtered hot, and the purplish blue filtrate formed was left at room temperature for 48 hours. The solid formed was filtered and dried in a warm oven (60°C) for three days to give a greenish blue powder.

The ionisation step was not attempted as the intended complex was not formed (refer to **Chapter 4)**

3.1.2 [Cu_2(*p*-$H_3NC_6H_4COO)_2(CH_3(CH_2)_{14}COO)_2]X_2$

(a) One-pot synthesis (X = Cl)

$CH_3(CH_2)_{14}COOH$ (5.00 g, 19.5 mmol) and *p*-$H_2NC_6H_4COOH$ (2.67 g, 19.5 mmol) were dissolved in CH_3CH_2OH by gentle heating. $CuCl_2.2H_2O$ (3.32 g, 19.5 mmol) was added to the solution, immediately forming a green solid in a green solution. The mixture was magnetically stirred and gently heated for 30 min. It was then left at room temperature overnight. NH_3 (30 ml) was added to the mixture and stirred overnight at room temperature. The mixture was heated until the smell of NH_3 could not be detected (about 30 minutes). The fine greenish blue powder formed was filtered from the warm reaction mixture, washed with CH_3CH_2OH followed by CH_3COCH_3, and dried in a warm oven (60°C). The yield was 6.76 g (73.2 %).

(b) Ligand-exchange Reaction (X = CF_3SO_3)

The ligand-exchange reaction involved reacting [Cu_2(*p*-$H_2NC_6H_4COO)_4$] with [$Cu_2(CH_3(CH_2)_{14}COO)_4$] (prepared in **Section 3.1.1(b)**).

(i) Synthesis of [$Cu_2(p\text{-}H_2NC_6H_4COO)_4$]

The procedure was similar as for [Cu_2(*p*-$HOC_6H_4COO)_4$] (**Section 3.1.1(b))**, replacing *p*-HOC_6H_4COOH with *p*-$H_2NC_6H_4COOH$ (6.90 g, $5.0x10^{-2}$ mmol). The product was a dark green powder, and the yield was 7.59 g (90.4 %).

(ii) Synthesis of [$Cu_2(p\text{-}H_2NC_6H_4COO)_2(CH_3(CH_2)_{14}COO)_2$]

The procedure was similar as for [Cu_2(*p*-$HOC_6H_4COO)_2(CH_3(CH_2)_{14}COO)_2$] **(Section 3.1.1(b))**, using [$Cu_2(CH_3(CH_2)_{14}COO)_4$] (0.50 g, 0.44 mmol) and [Cu_2(*p*-$H_2NC_6H_4COO)_4$] (0.29 g, 0.44 mmol). The product was a greenish blue powder.

***Step 5**. Ionisation of [$Cu_2(p\text{-}H_2NC_6H_4COO)_2(CH_3(CH_2)_{14}COO)_2$]*

This step was not attempted as the intended complex was not formed in step ***(ii)*** (refer to **Chapter 4**).

(c) Carbonate-base-acid reaction for the synthesis of [$Cu_2(p\text{-}H_2NC_6H_4COO)_2$ $(CH_3(CH_2)_{14}COO)_2$]

The procedure was the same as **Section 3.1.1(c)**, using $CH_3(CH_2)_{14}COOH$ (5.50 g, 21.4 mmol), *p*-$H_2NC_6H_4COOH$ (2.93 g, 21.4 mmol), and $CuCO_3.Cu(OH)_2$ (4.76 g, 21.4 mmol). The product was a greenish blue powder.

The ionisation step was also not attempted as the intended complex was not formed (refer to **Chapter 4)**

3.2 COPPER(II) MIXED CARBOXYLATES OF LOWER SYMMETRY

The next part of the project was continued with the syntheses of lower symmetry complexes. These were done in order to reduce the melting temperatures of these complexes to less than 100°C, so as to meet the definition of ionic liquids. Based on the method development performed earlier, the anionic copper(II) complex was prepared using the one-pot and ligand-exchange reaction, while the cationic copper(II) complex was prepared using the one-pot reaction only. The arylcarboxylate:alkylcarboxylate ratio was changed from 1:1 to 1:3.

3.2.1 $K[Cu_2(p\text{-}OC_6H_4COO)(CH_3(CH_2)_{14}COO)_3]$

a) One-pot synthesis

The procedure was the same as for $K_2[Cu_2(p\text{-}OC_6H_4COO)_2(CH_3(CH_2)_{14}COO)_2]$ **(Section 3.1.1(a),** using $p\text{-}HOC_6H_4COOH$ (0.90 g, 6.5 mmol) and $CH_3(CH_2)_{14}COOH$ (5.00 g, 19.5 mmol). The product was a fine turquoise blue powder, and the yield was 4.65 g (66.9 %)

b) Ligand-exchange reaction

The procedure for the synthesis of $[Cu_2(p\text{-}HOC_6H_4COO)(CH_3(CH_2)_{14}COO)_3]$ was the same for $[Cu_2(p\text{-}HOC_6H_4COO)_2(CH_3(CH_2)_{14}COO)_2]$ **(Section 3.1.1(b)**, using $[Cu_2(p\text{-}HOC_6H_4COO)_4]$ (0.29 g, 0.44 mmol) and $[Cu_2(CH_3(CH_2)_{14}COO)_4]$ (0.87g, 1.31 mmol). The product was a greenish blue powder and the yield was 1.57 g (80.5 %).

The procedure for the ionisation to $K[Cu_2(p\text{-}OC_6H_4COO)(CH_3(CH_2)_{14}COO)_3]$ was the same as for $K_2[Cu_2(p\text{-}OC_6H_4COO)_2(CH_3(CH_2)_{14}COO)_2]$ **(Section 3.1.1(b)**, using $[Cu_2(p\text{-}HOC_6H_4COO)(CH_3(CH_2)_{14}COO)_3]$ (0.90 g, 0.80 mmol) and KOH (0.80 mmol; 20 ml). The product was a fine grey powder and the yield was 0.34 g (50.7 %).

3.2.2 One-pot synthesis of $[Cu_2(p\text{-}H_3NC_6H_4COO)(CH_3(CH_2)_{14}COO)_3]Cl$

The procedure was the same as for $[Cu_2(p\text{-}H_3NC_6H_4COO)_2(CH_3(CH_2)_{14}COO)_2]Cl_2$ **(Section 3.1.2(a),** using $p\text{-}H_2NC_6H_4COOH$ (0.89 g, 6.5 mmol) and $CH_3(CH_2)_{14}COOH$ (5.00 g, 19.5 mmol). The product was a fine light blue powder and the yield was 6.52 g (72.5 %)

3.3 LOW SYMMETRY COPPER(II) MIXED CARBOXYLATES WITH SHORTER ALKYL CHAIN LENGTH

The project was then continued with the preparation and characterization of lower symmetry anionic copper(II) mixed carboxylate complexes with different alkyl chain length. This was done in order to further reduce the melting point.

The method used was ligand-exchange reaction, which was expected to form an intermediate complex, $[Cu_2(p\text{-}HOC_6H_4COO)(CH_3(CH_2)_nCOO)_3]$, where n = 10, 8 and 6. The intermediate complexes were then ionised using KOH as previously discussed.

3.3.1 $K[Cu_2(p\text{-}HOC_6H_4COO)(CH_3(CH_2)_{10}COO)_3]$

The procedure for the preparation of $[Cu_2(p\text{-}HOC_6H_4COO)(CH_3(CH_2)_{10}COO)_3]$ was the same as **Section 3.1.1(b)**, using $[Cu_2(p\text{-}HOC_6H_4COO)_4]$ (0.59 g, 0.87 mmol) and $[Cu_2(CH_3(CH_2)_{10}COO)_4]$ (2.41 g, 2.61 mmol). The product was a greenish blue powder and the yield was 2.51 g (82.0 %).

The procedure for the ionisation of $[Cu_2(p\text{-}HOC_6H_4COO)(CH_3(CH_2)_{10}COO)_3]$ to $K[Cu_2(p\text{-}OC_6H_4COO)(CH_3(CH_2)_{10}COO)_3]$ was similar as in **Section 3.1.1(b)**, using $[Cu_2(p\text{-}HOC_6H_4COO)(CH_3(CH_2)_{10}COO)_3]$ (1.00 g, 1.71 mmol) and KOH (1.71 mmol; 20 ml). The product was a dark green powder and the yield was 0.39 g (33.9 %).

3.3.2 K[Cu_2(*p*-OC_6H_4COO)($CH_3(CH_2)_8COO$)$_3$]

The procedure was the same as for K[Cu_2(*p*-OC_6H_4COO)($CH_3(CH_2)_{10}COO$)$_3$] (**Section 3.3.1**, using [Cu_2(*p*-HOC_6H_4COO)$_4$] (0.59 g, 0.87 mmol), [$Cu_2(CH_3(CH_2)_8COO)_4$] (2.12 g, 2.61 mmol) which formed [Cu_2(*p*-HOC_6H_4COO)($CH_3(CH_2)_8COO$)$_3$] as a greenish blue powder (2.35 g; 81.9 %).

K[Cu_2(*p*-OC_6H_4COO)($CH_3(CH_2)_8COO$)$_3$] was obtained as a black powder (0.37 g, 72.5 %) from the reaction of [Cu_2(*p*-HOC_6H_4COO)($CH_3(CH_2)_8COO$)$_3$] (0.51 g, 0.61 mmol) with KOH (0.61 mmol; 20 ml).

3.3.3 K[Cu_2(*p*-HOC_6H_4COO)($CH_3(CH_2)_6COO$)$_3$]

The procedure was the same as for K[Cu_2(*p*-OC_6H_4COO)($CH_3(CH_2)_{10}COO$)$_3$] (**Section 3.3.1**, using [Cu_2(*p*-HOC_6H_4COO)$_4$] (0.59 g, 0.87 mmol), [$Cu_2(CH_3(CH_2)_6COO)_4$] (1.83 g, 2.61 mmol) which formed [Cu_2(*p*-HOC_6H_4COO)($CH_3(CH_2)_6COO$)$_3$] as a greenish sticky solid (2.38 g; 75.8 %).

K[Cu_2(*p*-OC_6H_4COO)($CH_3(CH_2)_6COO$)$_3$] was obtained as a black powder (0.18 g, 25.0 %) from the reaction of [Cu_2(*p*-HOC_6H_4COO)($CH_3(CH_2)_6COO$)$_3$] (1.00 g, 1.28 mmol) with KOH (1.28 mmol; 20 ml).

3.4 THE C-C BOND-FORMING REACTION

The final stage was to ascertain if the ionic complexes may be used as catalysts in the C-C bond-forming reaction of methyl ketones. The complex chosen was **Complex 1** and **Complex 4**, and the methyl ketone chosen was 3,3-dimethyl-2-butanone.

3.4.1 Complex 1

K_2[Cu_2(*p*-OC_6H_4COO)$_2$($CH_3(CH_2)_{14}COO$)$_2$(*p*-HOC_6H_4COOH)$_2$].$2H_2O$ (**Complex 1)** (1.01 g) and 3,3-dimethyl-2-butanone (25 ml) were mixed in a round-bottomed flask. Concentrated hydrochloric acid was added dropwise to the mixture until the solids dissolved (15 ml). The orange brown solution formed was refluxed in an oil bath for four hours. The dark brown mixture formed was then cooled to room temperature overnight.

The excess unreacted ketone was then distilled off from the mixture. A dark brown (1.71 g) and yellow (6.04 g) fractions were collected after the unreacted ketone (clear solution) has distilled over. Both fractions were analyzed by GCMS.

3.4.2 Complex 4

Similarly as **Section 3.4.1**, $K[Cu_2(p\text{-}OC_6H_4COO)(CH_3(CH_2)_{14}COO)_3]$ (**Complex 4)** reacted with 3,3-dimethyl-2-butanone to produce dark brown (0.66 g) and yellow (2.29 g) fractions. Both fractions were also analyzed by GCMS.

3.5 INSTRUMENTAL ANALYSES

The product of each reactions were characterised by elemental analyses, FTIR, UV-Vis, TGA, DSC, OPM, room temperature magnetic susceptibility and cyclic voltammetry. The product of the C-C bond-forming reaction was analysed by GCMS.

3.5.1 Elemental Analyses

The elemental analysis of carbon, hydrogen and nitrogen was done using Perkin Elmer, PE 2400 Series II CHNS/O analyzer and Thermo Finnigan Flash EA 110. The pre-weighed samples (1.0 – 1.5 mg) were wrapped in tin capsules and were injected into a combustion chamber.

3.5.2 Fourier Transform Infrared Spectroscopy

The FTIR spectrum was recorded as a KBr pellet in the region 4000–400 cm^{-1} on a Perkin-Elmer FTIR SPECTRUM RX 1 Spectrometer.

KBr (spectroscopic grade) was heated in an oven for 24 hours at 120^oC and allowed to cool. A spatula full of KBr was placed in an agate mortar and grounded to a fine powder. A small amount of the sample was added and grounded with the KBr until a uniform mixture was obtained. The mixture was pressed into a pellet by applying high pressure. The pellet obtained was inserted into the spectrometer cell holder and the spectrum was recorded. The spectrum obtained was calibrated against KBr pellet as the background.

3.5.3 UV-Vis Spectroscopy

The electronic spectrum was recorded using Shimadzu UV-vis-NIR 3600 Spectrophotometer. The sample (0.01 g) was placed in a 10-ml volumetric flask, dissolved in CH_3OH-CH_3COOH (95:5 v/v). The solution was transferred into a 1 cm quartz cuvette, and the cuvette was wiped clean before putting it into the spectrometer holder. The spectrum was recorded against the solvents as blank.

The spectra for solid samples were obtained using the reflectance attachment of the same instrument, and employing $BaSO_4$ as the standard. Both spectra were recorded from 300 nm to 1000 nm.

3.5.4 Thermogravimetry

Thermogravimetric analysis (TGA) was performed on Pyris Diamond TG/DTA Perkin-Elmer instrument. The weight of sample (approximately 3-5 mg) in ceramic pan was initially recorded by a microbalance. The sample was then placed inside the TGA instrument and heated from room temperature to 900^{o}C with a scan rate of 10^{o}C/min under nitrogen gas purging at a flow rate of 20 cm^3/min.

3.5.5 Differential Scanning Calorimetry

The weight of the sample in aluminium pan was initially recorded by microbalance. The sample pan was then placed inside the Perkin Elmer DSC 6 instrument. The temperature range was set from room temperature to 300^{o}C with the scan rate 10^{o}C/min under N_2 gas purging at a flow rate of 10 cm^3/ min.

3.5.6 Optical Polarizing Microscopy

The phase transitions were observed on an Olympus BX51 polarizing microscope equipped with a Mettler Toledo FP90 method controller and FP82HT hot stage. The temperature was set at 30^{o}C to around 200^{o}C (below T_{dec} of sample), and the heating and cooling rates adjusted at between 2^{o}C to 5°C min^{-1}. The magnification was 50x.

A thin layer of the powder was placed on the slide and then on the microscope hot stage holder. The sample was brought into focus by adjusting the coarse adjustment. The parameters were set and the phase changes were recorded.

3.5.7 Magnetic Susceptibility

The room temperature magnetic susceptibility was measured using the Gouy method, and performed on a Sherwood Auto Magnetic Susceptibility Balance. The length of sample tube and weight of sample were initially recorded for the conversion of χ_v to χ_g. The sample was grounded to a fine powder in a mortar and pestle.

A small amount of the powdered sample was placed in the tube and tapped to the bottom of the tube. The closed end of the tube was tapped for about a minute on two sheets of filter paper on a wooden bench. This process was continued until the tube was filled to the mark. Any excess compound was wiped away from the mouth of the tube using a soft tissue. The tube was then placed inside the Gouy balance, and the χ_g value was recorded from the reading on the instrument.

The calculated magnetic moment, μ_{eff}, was calculated using formula $\mu_{eff} = 2.824[T(\chi_m^{corr} - N\alpha)]^{½}$ B.M. The diamagnetic correction was made using Pascal's constant, and the temperature-independent paramagnetism ($N\alpha$) was taken as 60 x 10^{-6} c.g.s e.m.u for each copper(II) ion.

3.5.8 Cyclic Voltammetry

The cyclic voltammetry was performed on a Gamry Potentiostat/ Galvanostat 600 instrument, using a standard three-electrode assembly (glassy carbon as the working electrode, platinum wire as the counter electrode, and saturated calomel as the reference electrode). The supporting electrolyte used was tetrabutylammonium tetrafluoroborate (TBATFB) and the solvent was CH_3OH-CH_3COOH (95:5 v/v). The molarity of the electrolyte and sample were 0.1 M and 1.5x 10^{-3} M, respectively. The initial potential range was +1.5 V to -1.5 V and the scan rate was 50 mV s^{-1}. The working electrode was polished with alumina before and after used and the sample solution was bubbled with N_2 gas prior to measurement.

3.5.9 Gas Chromatography-Mass Spectroscopy

The mass spectrum was recorded in acetone or methanol on a Perkin-Elmer Clarus 600 GCMS with Elite-5MS capillary column with dimension 30 m (L) x 0.25 mm (ID) x 0.25 µm (DF), or on a Shimadzu GCMS-QP2010 Plus with RTx®-5MS capillary column having dimension 30 m (L) x 0.25 mm(ID) x 0.25 µm (DF). (L = length, ID = inner diameter, DF= film thickness).