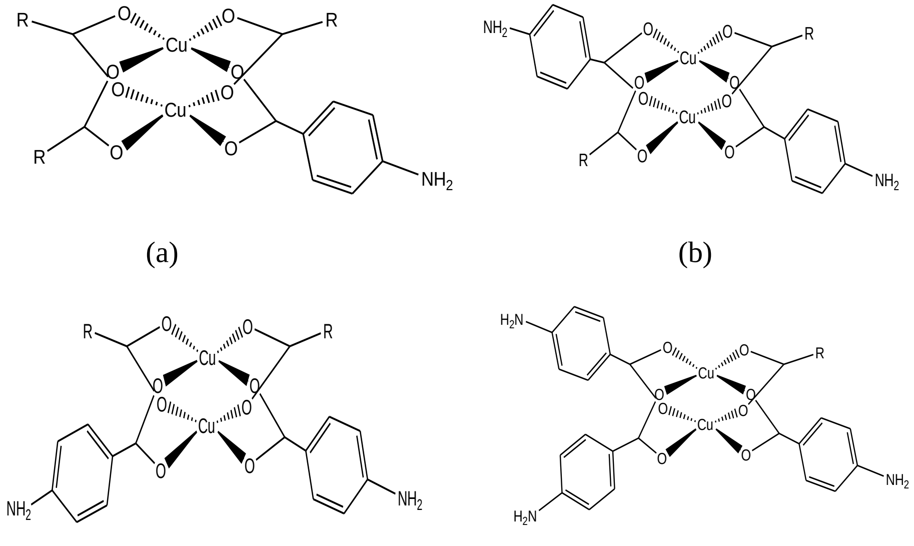
CHAPTER 3. EXPERIMENTAL

3.1 MATERIALS

As stated in **Chapter 1**, the main objective of this research was to synthesize and characterize copper(II) mixed carboxylates as low-temperature, thermally-stable, magnetic and redox-active metallomesogens. Thus, six copper(II) mixed carboxylates with the intended general formula $[Cu_2(p\text{-}H_2NC_6H_4COO)_n(CH_3(CH_2)_{14}COO)_{4-n}]$, where n is 1-3, were synthesized by the one-pot method [1]. The expected structural formulas for these complexes are shown in **Figure 3.1**.



(a) (b)

(c) (d)

Figure 3.1 *The expected structural formulas of complexes prepared in this project* (R = $CH_3(CH_2)_{14}$)*: (a) n = 1; (b) n = 2, trans-isomer; (c) n = 2, cis-isomer; and (d) n = 3*

The copper(II) salts used to prepare the complexes were copper(II) nitrate trihydrate ($Cu(NO_3)_2.3H_2O$; FW 241.6 g/mol), anhydrous copper(II) chloride

($CuCl_2$; FW 134.5 g/mol), copper(II) sulphate pentahydrate ($CuSO_4.5H_2O$; FW 249.7 g/mol), and copper(II) ethanoate monohydrate ($[Cu(CH_3COO)_2].H_2O$; FW 199.7 g/mol). The carboxylic acids used were hexadecanoic acid, ($CH_3(CH_2)_{14}COOH$; FW 256.4 g/mol) and *p*-aminobenzoic acid (*p*-$H_2NC_6H_4COOH$; FW 137.14 g/mol). The main solvent used was ethanol. All chemicals were commercially available and used as received.

The complexes were characterized by CHN elemental analyses, FTIR and UV-vis spectroscopies, molar conductivity, TGA, DSC, OPM, room-temperature magnetic susceptibility, cyclic voltammetry, and for crystalline sample by single crystal X-ray crystallography.

3.2 SYNTHESIS OF $[Cu_2(p\text{-}H_2NC_6H_4COO)_2(CH_3(CH_2)_{14}COO)_2]$

Different copper(II) salts were used in the synthesis in an attempt to find the most suitable salt that would form the complex with the intended chemical and structural formula, and in good yield.

3.2.1 Reaction between $Cu(NO_3)_2$, $p\text{-}H_2NC_6H_4COOH$ and $CH_3(CH_2)_{14}COOH$

$Cu(NO_3)_2.3H_2O$ (5.6920 g, 23.6 mmol) was added to 100 ml of hot ethanolic solution of *p*-$H_2NC_6H_4COOH$ (3.2202 g, 23.5 mmol) and $CH_3(CH_2)_{14}COOH$ (6.0514 g, 23.5 mmol). The green solution formed was cooled and an excess NH_3 (30%) was added dropwise, forming a purple solution. The solution was magnetically stirred at room temperature overnight, and the excess NH_3 removed by gentle heating. Two products were isolated from the reaction mixture.

Complex 1 was a pale blue powder which deposited from the hot reaction mixture. The yield was 5.1661 g, and the results of the elemental analyses were 59.24% C, 10.92% H, and 2.48% N.

Complex 2 was isolated as a dark green powder from the filtrate on complete removal of the solvent. The yield was 1.7251 g, and the results of the elemental analyses were 48.89% C, 3.80% H and 9.17% N.

3.2.1.1 Reaction of ***Complex 1*** *with 2,2'-bipyridine*

A mixture of **Complex 1** (1.0717 g) and 2,2'-bipyridine (0.1874 g) was gently heated in CH_3OH-CH_3CH_2OH (1:2) for 30 minutes. The black solid formed in a dark blue solution was filtered off. On standing overnight, small blue crystals deposited out from the filtrate (0.5483 g; 69%). It was recrystallized from methanol-THF (1:1) to give dark blue block crystals after two weeks at room temperature. The results of the elemental analyses were 70.01% C; 10.63% H, and 4.13% H. Single crystal X-ray crystallography identified it as bis(μ-hexadecanoato-$\kappa^2 O:O$)bis[(2,2'-bipyridine-$\kappa^2 N,N'$)(hexadecanoato-κO)copper(II)], structural formula, $[Cu_2(CH_3(CH_2)_{14}COO)_4(C_{10}H_8N_2)_2].2CH_3OH$ [2].

3.2.2 Reaction between $Cu(CH_3COO)_2$, p-$H_2NC_6H_4COOH$ and $CH_3(CH_2)_{14}COOH$

The method was the same as 3.2.1, using $[Cu(CH_3COO)_2].H_2O$ (1.5865 g; 7.95 mmol), p-$H_2NC_6H_4COOH$ (1.1078 g; 8.08 mmol) and $CH_3(CH_2)_{14}COOH$ (2.0196 g; 7.88 mmol). Two products were obtained from the reaction mixture.

Complex 3 was a dark green powder which deposited from the hot reaction mixture. The yield was 0.6930 g, and the results of the elemental analyses were 52.23% C, 5.11% H, and 6.48% N.

A pale blue powder deposited from the reaction mixture on standing at room temperature after a few days was similar to **Complex 1**. The yield was 2.3457 g and the results from the elemental analyses were 59.93% C, 11.28% H and 2.19% N.

3.2.3 Reaction between $CuSO_4$, p-$H_2NC_6H_4COOH$ and $CH_3(CH_2)_{14}COOH$

The method was the same as 3.2.1, using $CuSO_4.5H_2O$ (2.2162 g; 8.88 mmol), *p*-$H_2NC_6H_4COOH$ (1.1181 g; 8.15 mmol) and $CH_3(CH_2)_{14}COOH$ (2.0549 g; 8.01 mmol).

The product deposited as a pale blue powder from the hot reaction mixture was similar to **Complex 1.** The yield was 2.1341 g and the results of the elemental analyses were 58.72% C, 10.98% H and 1.96% N.

3.2.4 Reaction between $CuCl_2$, p-$H_2NC_6H_4COOH$ and $CH_3(CH_2)_{14}COOH$

The method was the same as 3.2.1, using $CuCl_2$ (1.0738 g; 8.00 mmol), *p*-$H_2NC_6H_4COOH$ (1.0973 g; 8.01 mmol) and $CH_3(CH_2)_{14}COOH$ (2.0546 g; 8.01 mmol). Two products were obtained from the reaction mixture (**Complex 4** and **Complex 5**).

Complex 4 was a pale green powder deposited from the hot reaction mixture. The yield was 0.7279 g, and the results of the elemental analyses were 32.78% C, 4.76% H and 8.12% N.

Complex 5 was isolated as a dark green powder from the filtrate on complete removal of the solvent. The yield was 0.2516 g, and the results of the elemental analyses were 54.75% C, 7.78% H and 6.93% N.

3.3. SYNTHESIS OF $[Cu_2(p\text{-}H_2NC_6H_4COO)(CH_3(CH_2)_{14}COO)_3]$

The method used was the same as 3.2.4, using $[Cu(CH_3COO)_2].H_2O$ (2.8865 g; 14.46 mmol), p-$H_2NC_6H_4COOH$ (0.9663 g; 7.05 mmol) and $CH_3(CH_2)_{14}COOH$ (5.4101 g; 21.10 mmol). Two products were obtained from the reaction mixture.

Complex 6 was a pale blue powder which deposited from the hot reaction mixture. The yield was 4.4785 g and the results of the elemental analyses were 60.12% C, 10.83% H, and 2.07% N.

A dark green powder was isolated as from the filtrate on complete removal of the solvent was similar to **Complex 3**. The yield was 0.2984 g and the results of the elemental analyses were 62.30% C, 9.66% H and 5.03% N.

3.4 SYNTHESIS OF $[Cu_2(p\text{-}H_2NC_6H_4COO)_3(CH_3(CH_2)_{14}COO)]$

The method was the same as 3.2.4, using $[Cu(CH_3COO)_2].H_2O$ (2.8011 g; 14.03 mmol), p-$H_2NC_6H_4COOH$ (2.8911 g; 21.08 mmol) and $CH_3(CH_2)_{14}COOH$ (1.8065 g; 7.46 mmol). Two products were obtained from the reaction mixture.

A dark green powder was which deposited from the hot reaction mixture was similar to **Complex 3.** The yield was 0.8985 g, and the results of the elemental analyses were 50.05% C, 5.34% H and 6.65% N.

A pale blue power was isolated from the filtrate on complete removal of the solvent was similar to **Complex 1**. The yield was 1.4308 g and the results of the elemental analyses were 59.80% C, 11.66% H, and 2.14% N.

3.5 CHARACTERIZATIONS

The complexes were characterized by elemental analyses, Fourier transform infrared spectroscopy (FTIR), electronic spectroscopy (UV-vis), molar conductivity, thermogravimetry (TGA), differential scanning calorimetry (DSC), optical polarized microscopy (OPM), magnetic susceptibility, and cyclic voltammetry (CV).

3.5.1 Elemental Analyses

The elemental analysis was obtained using the CHNS/O Series II 2400. The sample was placed in a thin aluminium sample holder. The weight of the sample (about 1.5 mg) was recorded using AD-6 ultramicrobalance. The weighed sample was then folded to smaller size to fit in the column. The time taken for complete analysis was 6 minutes.

3.5.2 Fourier Transform Infrared Spectroscopy

The FTIR spectrum was recorded from 4000 cm^{-1} to 400 cm^{-1} on a Perkin-Elmer FTIR SPECTRUM RX 1 spectrometer. The analysis was either done on a neat sample or as potassium bromide (KBr) disc.

The KBr powder was heated in an oven overnight at 120^{o}C and allowed to cool in a dessicator. The powder was grinded, pressed into transparent disc and scanned as a background. The complex (1 part) and KBr (9 part) were grind together to a fine powder using a mortal and pestle, and then pressed into a transparent disc.

3.5.3 Ultraviolet-Visible Spectroscopy

The solution UV-vis spectra of the complexes were recorded from 300 nm to 1000 nm on a Shimadzu 1500 UV-VIS spectrometer in 1-cm quartz cells. The solvents were dimethylsulfoxide (DMSO) mixed with a few drops of acetic acid or chloroform ($CHCl_3$).

The UV-vis spectra of solid samples were recorded from 300 nm to 1000 nm on a Shimadzu 3600 UV-VIS-NIR spectrophotometer using the reflectance technique. The standard was $BaSO_4$. The complexes were pressed in the provided compartment using a broad glass rod.

3.5.4 Molar Conductivity

The molar conductivity were measured using a Cyberscan CON510 Bench Conductivity/TDS Meter. An exactly known amount of the complex was dissolved in DMSO (with three drops of ethanoic acid added to dissolve the complex) in a 50-mL volumetric flask, and its conductance (κ) measured. The conductance of the blank was also recorded. The value of the molar conductance (Λ_M) was calculated using the equation: $\Lambda_M = (1000\ \kappa)/M$, where κ is the conductance and M is the molarity.

3.5.5 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was performed from 50-900^{o}C on a Perkin-Elmer Pyris Diamond TG/DTA Thermal System under nitrogen atmosphere at a flow rate of 20 cm^{3} min^{-1} and scan rate of 20^{o}C min^{-1}. For the analysis, the complex was grind to a fine powder, and then about 2-3 mg of the complex was introduced into a ceramic crucible.

3.5.6 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was performed from 35-300^{o}C on a Perkin-Elmer DSC 6 under nitrogen atmophere at a flow rate of 10 cm^{3} min^{-1} and scan rate of 10^{o}C min^{-1}. For the analysis, the complex was grind to a fine powder, and then about 2-3 mg of the complex was introduced into an aluminium crucible ceramic.

3.5.7 Optical Polarized Microscopy

The optical polarized microscopic (OPM) analysis was performed with an Olympus Polarizing Microscope equipped with a Mettler Toledo FP90 central processor and FN82HT hot stage. The complex was placed on a clean glass slide, and it was heated on the hot stage under polarized microscope at the scan rate of 5^{o}C min^{-1}. The magnification was 50X.

3.5.8 Room-Temperature Magnetic Susceptibility

The room-temperature magnetic susceptibility was recorded at 25^{o}C on a Sherwood Auto Magnetic Susceptibility Balance by the Gouy method, using $Hg[Co(SCN)_4]$ as the calibrant.

The complex was grind and packed into a clean and dry glass tube to the mark. The tube was then inserted into the balance. The length and the weight of the sample were recorded, and the values keyed-in into the instrument. The gram magnetic susceptibility reading was noted and was used to calculate the molar susceptibility, χ_m using the equation: $\chi_m = \chi_g$ x MW (where MW is the molecular weight).

The molar susceptibility was corrected for the diamagnetism of the constituent atoms using Pascal's constant (**Appendix 2**), and was used to calculate the effective dipole moment, μ_{eff}, using the following equation:

$$\mu_{eff} = 2.82[T(\chi_m^{corr} - N\alpha)]^{½}$$

3.5.9 Cyclic Voltammetry

Cyclic voltammetry (CV) was performed on a GAMRY Potentiostat/Galvanostat 600 instrument using a standard three-electrode assembly (glassy carbon as the working electrode, platinum as the counter electrode, and Ag/AgCl as the reference electrode). The supporting electrolyte was $(^nBu)_4NBF_4$ (0.1 M), and the scan rate was 100 mV s^{-1}. The weight of the complex was about 0.02 g and the weight of the electrolyte was about 0.2 g. The solvents were dimethylsulfoxide (DMSO) mixed with a few drops of acetic acid or chloroform ($CHCl_3$).

3.5.10 X-ray Crystallography

X-Ray crystallography was done using APEX2 (Bruker, 2009), cell refinement by SAINT (Bruker, 2009), data reduction by SAINT where the program(s) used to solve structure is SHELXS97 (Sheldrick, 2008); program(s) used to refine structure is SHELXL97 (Sheldrick, 2008); molecular graphics by XSEED

(Barbour, 2001) whereas the software used to prepare material for publication is publCIF (Westrip, 2010).

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