# CHAPTER 1 INTRODUCTION

Copper(II) alkylcarboxylates with long alkyl chains are thermotropic magnetic metallomesogens with low melting temperatures. An example is tetra(hexadecanoato)dicopper(II), $[Cu_2(CH_3)_{14}COO)_4]$, which showed a columnar hexagonal mesophase ($D_h$) and melted at 112$^oC$ [1]. These synergic properties (magnetism, mesomorphism, and low melting temperature) are useful as they enable the molecules of these materials to be aligned by the weaker magnetic field (compared to electric field required by organic liquid crystals) at low temperature, and to form thin films for molecular spintronic applications.

In addition, by reducing the molecular symmetry [2], their melting temperatures may be lowered further by substituting one of the alkylcarboxylates with arylcarboxylates with ionisable functional groups (example, $NH_2$ or OH), which may be easily converted to metal-containing ionic liquids (ionic compounds with melting temperatures less than 100$^oC$). Other strategies that can be adopted to reduce the melting points are to use carboxylate ions with long, preferably branch, hydrocarbon chains [1], and to use non-planar large counterions [3].

Carbon-carbon bond-forming reactions are examples of important organic syntheses. An example is aldol condensation of aldehydes and ketones, which can be induced by transition metal complexes [4]. Recently, it was discovered that copper(II) benzoate and its derivatives catalysed facile one-step carbon-carbon bond forming reactions between methyl ketones and aldehydes [5]. However, these reactions were limited to liquid ketones and/or aldehydes due to the involvement of organic compounds and inorganic hydrophobic reagents. To extend these important reactions to solid organic compounds, solvents that can dissolve both organics and inorganic

reactants are needed. Metal-containing ionic liquids may be able to function as solvents-cum-redox catalysts in such reactions.

Hence, this research project was focussed on the synthesis, characterisation, thermal, magnetic and redox properties 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 $CF_3SO_3$. These complexes were specially designed in order to study the effect of hydrocarbon chain length and reduced molecular symmetry on the melting temperatures.

Several methods were reported in the literature for the synthesis of copper(II) carboxylates. Examples are the reaction between Cu(II) salt (chloride, sulphate, and nitrate) with RCOONa [6-10], metathesis reaction between $Cu_2(RCOO)_4$ and R'COOH [1, 7, 10-14], reaction between $CuCO_3$ and RCOOH [15-17], and reaction between $Cu(OH)_2$ and RCOOH [18]. However, there was no specific method to prepare Cu(II) mixed carboxylates.

Hence, this project started with the method development to determine the best method for the synthesis of these complexes [19]. Three methods were chosen: one-pot synthesis, ligand-exchange reaction and carbonate-acid-base reaction. The complexes were characterised by elemental analyses, fourier transformed infrared spectroscopy (FTIR), ultraviolet-visible spectroscopy (UV-vis), thermogravimetry (TGA), optical polarised microscopy (OPM), differential scanning calorimetry (DSC), magnetic susceptibility (Gouy method), cyclic voltammetry (CV). As an addition, gas chromatography-mass spectroscopy (GCMS) was used to analyze the products formed from the carbon-carbon bond forming reaction.

The findings from this research were published in an ISI journal and presented either orally or poster at national / international conferences and seminars, listed below:

1. *Zaimatul ‘Azian Kamarazaman, Norbani Abdullah, Ahmad Nazeer Che Mat, Lailatun Nazirah Ozair and Tee Jia Tee, *Dinuclear Cu(II) Mixed Carboxylates as Thermally-Stable Magnetic Metallomesogens*, Mini Symposium, University of Malaya and Wagenigen University (oral) (Feb 22, 2011).
2. Lailatun Nazirah Ozair, Norbani Abdullah, Yatimah Alias, Zaimatul ‘Azian Kamarazaman, *Thermally-Stable Magnetic Metal-Based Ionic Liquid Precursors: $[Cu_2(p\text{-}HOC_6H_4COO)_2(RCOO)_2]$; R = $CH_3(CH_2)_{14}$, $CH_3(CH_2)_7CH(CH_2)_5$,* Bilateral Symposium, University of Malaya and Hydrabad University (poster) (Oct. 26-28, 2010).
3. *Zaimatul ‘Azian Kamarazaman, Norbani Abdullah, Yatimah Alias, *Synthesis and Characterization of $K[Cu_2(CH_3(CH_2)_{14}COO)_3(p\text{-}OC_6H_4COO)]$ as functional ionic liquids*, Seminar Nasional Himpunan Kimia Indonesia, Universitas Hasanuddin, Makassar, Indonesia (oral) (Aug 2-3, 2010).
4. *Zaimatul ‘Azian Kamarazaman, Norbani Abdullah, Yatimah Alias, *Synthesis and Characterization of $K_2[Cu_2(p\text{-}OC_6H_4COO)_2(CH_3(CH_2)_{14}COO)_2]$ and $K[Cu_2(CH_3(CH_2)_{14}COO)_3(p\text{-}OC_6H_4COO)]$ as functional ionic liquids*, Regional Conference on Ionic Liquids 2009, UMKL (oral) (Nov 24-25, 2009).
5. *Zaimatul 'Azian Kamarazaman, Norbani Abdullah and Yatimah Alias**,** *Copper(II) Mixed-Carboxylates as solvent-cum-catalyst Ionic Liquids, $[Cu_2(p\text{-}H_3NC_6H_4COO)_2(CH_3(CH_2)_nCOO)_2]Cl_2$ ; n=1, 2, 3, 4, 14 and 16*, ASIANALYSIS X - 10th. Asian Conference on Analytical Sciences 2009 (oral) **(**Aug 11-13, 2009).
6. *Norbani Abdullah, Zaimatul ‘Azian Kamarazaman, *Copper(II) Mixed-Carboxylates as Metal Containing Ionic Liquids*, NANO-SciTech-2008,

International Conference on Nanoscience and Nanotechnology, Nanotechnology, Shah Alam, Selangor (oral) (Nov 18-21, 2008).

7. N. Abdullah and Z.A. Kamarazaman, *AIP Conf. Proc., 1136, 361 (2009).*

8. *Zaimatul 'Azian Kamarazaman, Norbani Abdullah, and Yatimah Alias, *One-Pot Synthesis and Electrochemical Properties of* $K_2\{Cu_2[p\text{-}OC_6H_4COO]_2[CH_3(CH_2)_nCOO]_2\}$, SKAM 21st - Malaysian Analytical Chemistry Symposium, Kota Kinabalu, Sabah (poster) (Nov. 24-27, 2008).

The thesis has five chapters. **Chapter 1** covers the introduction of the project. **Chapter 2** contains the theory and review of metallomesogens and metal-containing ionic liquids, including brief reviews on copper(II) carboxylates and on the carbon-carbon bond-forming reactions. This chapter also contains the theories of instrumental analyses used in this work, as listed above. **Chapter 3** presents the experimental methods, divided into four main sections: method development, synthesis of copper(II) mixed carboxylates of lower symmetry, synthesis of low symmetry copper(II) mixed carboxylates with shorter alkyl chain length, and the carbon-carbon bond-forming reaction of selected complexes with a methyl ketone. It is then followed by techniques and parameters of the relevant instrumental analyses. **Chapter 4** presents the results and discussions, and **Chapter 5** presents the conclusions and suggestions for future works. A list of references is included at the end of each chapter.

**References**


[1] G. S. Attard and P. R. Cullum, *Liquid Crystals,* Vol. 8, No. 3, 299-309 (1990).

[2] R. Paschke, D. Balkow, and E. Sinni, *Inorganic Chemistry* (published on the web) (2001).

[3] P. Espinet, *Inorganica Chimica Acta* 361, 2270-2278 (2008).

[4] R.L. Bennett and M. I. Bruce, *Aust. J. Chem*., 28, 1141-3 (1975).

[5] N. Abdullah and M. H. Chisholm, *Role of $Cu_2(XC_6H_4COO)_4$ in facile C-C bond forming reaction of carbonyls*, International Conference on Molecular Chemistry, 54 (2008).

[6] J. Lewis and F. Mabbs, *Notes*, 3894-3897 (1965).

[7] W. E. Hatfield, C. S. Fountain, and R. Whyman, *Inorganic Chemistry*, Vol. 5, No. 11, 1855-1858 (1966).

[8] F. Cariati, L. Erre, G. Micera, A. Panzanelli, and P. Piu, *Thermochimica Acta,* 66 1-10 (1983).

[9] M. Inoue, M. Kishita, and M. Kubo, *Inorganic Chemistry*, Vol. 3, No. 2, 239-242 (1964)

[10] M. Inoue, M. Kishita, and M. Kubo, *Inorganica Chimica Acta*, 80, 57-65 (1983).

[11] L. Strinna Erre, G. Micera, P. Piu, F. Cariati, and G. Ciani, *Inorg. Chem*., 24, 2291-2300 (1985).

[12] L. S. Erre and G. Micera, *Polyhedron* Vol. 6, No. 10, 1869-1874 (1987).

[13] S.P. Perlepes, E.Libby, W. E. Streib, K. Folting and G. Christou, *Polyhedron* Vol. 11, No. 8, 923-936 (1992).

[14] W. Zhang, S. Liu, C. Ma and D. Jiang, *Polyhedron*, Vol. 17, No. 22, 3835-3839 (1998).

[15] Y. Rodriguez-Martin, J. Sanchiz, C. Ruiz-Perez, F. Lloret, M. Julve, *Inorganica Chimica Acta* 326, 20-26 (2001).

[16] D. Choquesillo-Lazarte, B. Covelo, J. M. González-Pérez, A. Castiñeiras, and J. Niclós-Gutiérrez, *Polyhedron* 21, 1485-1495 (2002).

[17] T. Kawata, H. Uekusa, S. Ohba, T. Furukawa, T. Tokii, Y. Muto, and M. Kato, *Acta. Cryst*. B48, 253-261(1992).

[18] M. Devereux, D. O'Shea, M. O'Connor, H. Grehan, G. Connor, M. McCann, G. Rosair, F. Lyng, A. Kellett, M. Walsh, D. Egan and B. Thati, *Polyhedron* 26, 4073-4084 (2007).

[19] N. Abdullah and Z.A. Kamarazaman, *AIP Conf. Proc.*, 1136, 361 (2009).