

**SYNTHESIS AND CHARACTERISATION OF
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AND
 $[Cu_2(p-H_3NC_6H_4COO)_a(CH_3(CH_2)_nCOO)_{4-a}]X_a$
AND THEIR REACTIONS WITH SELECTED
KETONES**

ZAIMATUL 'AZIAN KAMARAZAMAN

**FACULTY OF SCIENCE
UNIVERSITY OF MALAYA
KUALA LUMPUR**

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**DISSERTATION SUBMITTED IN FULFILLMENT
OF THE REQUIREMENT FOR
DEGREE OF MASTER OF SCIENCE**

**DEPARTMENT OF CHEMISTRY
FACULTY OF SCIENCE
UNIVERSITY OF MALAYA
KUALA LUMPUR**

2012

ACKNOWLEDGEMENTS

Alhamdulillah, I praise and thank Allah SWT for His greatness and for giving me the strength and courage to complete this thesis.

First and foremost I offer my sincerest gratitude to my supervisor, Assoc. Prof. Dr. Norbani Abdullah, who has supported me throughout my thesis with her patience and expertise while allowing me the room to work on my own way. I attribute my Master degree to her encouragement and effort and without her this thesis would not have been completed. One simply could not wish for a better or friendlier supervisor.

Deepest gratitude are also due to Prof. Dr. Yatimah Alias, my second supervisor, and Assoc. Prof. Dr. Zunita Zakaria who encouraged and advised me to continue my Master degree even after 15 years 'away' from chemistry line.

In my daily work I have been blessed with a friendly and cheerful group of friends. Special thanks to all my group members for sharing the literature and invaluable assistance. Not forgetting to all staff in Chemistry Department, Faculty of Science, University of Malaya. Without their cooperation and kindness, this project could not have been completed.

My parents, Kamarazaman Hj. Hasan and Mahawiyah Khalid deserve special mention for their inseparable support and prayers. Words fail to express my appreciation to my husband, Mr. Amal Nathan whose dedication, love and confidence in me, has taken the load off my shoulder.

Finally, I would like to thank everybody who was important to the successful realization of this thesis, as well as expressing my apology that I could not mention personally one by one.

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ABSTRACT

This research focussed on the development of the synthetic methods and characterisation (structural, thermal, magnetic and redox properties) of two types of ionic copper(II) mixed-carboxylates: (a) $K_a[Cu_2(p-OC_6H_4COO)_a(CH_3(CH_2)_nCOO)_{4-a}]$, and (b) $[Cu_2(p-H_3NC_6H_4COO)_a(CH_3(CH_2)_{14}COO)_{4-a}]X_a$, where $a = 1, 2$; $n = 14, 10, 8$, and 6; $X = Cl, CH_3COO$ and CF_3SO_3 . These complexes were designed to be thermally stable and magnetic metallomesogens and/or metal-containing ionic liquids.

The synthetic methods used to prepare these complexes were one-pot reaction, ligand-exchange reaction, and acid-carbonate-base reaction. A total of twelve (12) complexes were successfully prepared and fully characterised (**Table 1**).

Table 1 The structural formulas of the complexes

Complex	Structural formula
1	$K_2[Cu_2(p-OC_6H_4COO)_2(CH_3(CH_2)_{14}COO)_2(p-HOC_6H_4COOH)_2].2H_2O$
2	$[Cu_2(p-HOC_6H_4COO)_2(CH_3(CH_2)_{14}COO)_2(CH_3(CH_2)_{14}COOH)(H_2O)].CH_3CH_2OH$
3	$[Cu_2(p-H_2NC_6H_4COO)_2(CH_3(CH_2)_{14}COO)_2].2H_2O$
4	$K[Cu_2(p-OC_6H_4COO)(CH_3(CH_2)_{14}COO)_3]$
5	$[Cu_2(p-HOC_6H_4COO)(CH_3(CH_2)_{14}COO)_3(CH_3CH_2OH)_2]$
6	$[Cu_2(p-HOC_6H_4COO)(CH_3(CH_2)_{10}COO)_3].H_2O$
7	$[Cu_2(p-HOC_6H_4COO)(CH_3(CH_2)_8COO)_3].CH_3CH_2OH$
8	$[Cu_2(p-HOC_6H_4COO)(CH_3(CH_2)_6COO)_3(CH_3(CH_2)_6COOH)(CH_3CH_2OH)].H_2O$
9	$[Cu_2(CH_3(CH_2)_{14}COO)_2(OH)_2(H_2O)_4].2C_2H_5OH$
10	$K_2[Cu_2(CH_3(CH_2)_{10}COO)_2(OH)_4]$
11	$K_2[Cu_2(CH_3(CH_2)_8COO)_2(OH)_4]$
12	$K_2[Cu_2(CH_3(CH_2)_6COO)_2(OH)_4]$

The structural formulas of these complexes were deduced from elemental analyses, FTIR and UV-vis spectroscopies. The thermal properties were determined by TGA and DSC, while the mesomorphic properties were determined by OPM. The magnetic properties were determined by Gouy method using a magnetic susceptibility balance, and the redox properties by cyclic voltammetry. Additionally, GCMS was used to analyze the products formed from the carbon-carbon bond-forming reaction of methyl carbonyl (3,3-dimethyl-2-butanone).

The structure of most of the complexes were dimeric paddle-wheel with either square planar or square pyramidal geometry at copper(II) centres.

Complex 1 had the highest thermal stability ($T_{\text{dec}} = 424^{\circ}\text{C}$) compared to the other complexes ($T_{\text{dec}} = 200^{\circ}\text{C} - 250^{\circ}\text{C}$). Additionally, the complexes with a higher ratio of the alkylcarboxylate ligands (aromatic: aliphatic = 1:3) were more thermally stable; the stability increases with increasing alkyl chain length. However, the opposite trend was noted for the melting temperatures: complexes with a higher ratio of the alkylcarboxylate ligands had a lower melting point.

Six of the complexes (**Complex 2, Complexes 5 - 9**) exhibited metallomesogenic properties. However, the type of mesophase cannot be deduced with certainty from OPM.

All complexes were magnetic at room-temperature. Except for **Complex 1** which showed a weak ferromagnetic interaction ($\mu_{\text{eff}} = 3.12 \text{ B.M.}; 2J = 60 \text{ cm}^{-1}$), the other complexes had magnetism ($\mu_{\text{eff}} = 1.87 \text{ B.M.} - 2.62 \text{ B.M.}$) which were lower than the spin-only value for two unpaired electrons ($\mu_{\text{eff}} = 2.83 \text{ B.M.}$), with variable strength of antiferromagnetic interaction ($2J = -78 \text{ cm}^{-1}$ to -346 cm^{-1}). The complexes with a higher ratio of the alkylcarboxylate ligands have a stronger antiferromagnetic interaction. However, the difference in the chain length did not have much effect on the magnetic interaction.

All of the complexes were redox-active and showed step-wise quasi-reversible electrochemical reaction. The initial reduction potentials were in the range of 0.07-0.30 V.

Both **Complex 1** and **Complex 4** 'catalysed' the carbon-carbon bond-forming reaction of 3,3-dimethyl-2-butanone. **Complex 4** seemed to be a better 'catalyst' as the products formed were in higher purity and amount.

The findings of this research were published in one (1) ISI journal and presented either orally or as poster at three (3) national and four (4) international conferences and seminars (**Appendix 1**).

ABSTRAK

Penyelidikan ini berfokuskan pembangunan kaedah sintetik dan pencirian (struktur, dan sifat terma, magnet dan redoks) dua jenis kuprum(II) karboksilat bercampur ionik: (a) $K_a[Cu_2(p-OC_6H_4COO)_a(CH_3(CH_2)_nCOO)_{4-a}]$, dan (b) $[Cu_2(p-H_3NC_6H_4COO)_a(CH_3(CH_2)_{14}COO)_{4-a}]X_a$, dengan $a = 1, 2$; $n = 14, 10, 8$ dan 6 ; $X = Cl, CH_3COO$ dan CF_3SO_3 . Kompleks-kompleks ini direkabentuk untuk menjadi metallomesogen dan/atau cecair ionik yang stabil secara terma dan magnetik.

Kaedah sintesis yang digunakan untuk menyediakan kompleks-kompleks tersebut adalah tindak balas satu pot, tindak balas penukaran ligan, dan tindak balas asid-karbonat-bes. Sejumlah dua belas (12) kompleks berjaya disediakan dan dicirikan sepenuhnya (**Jadual 1**).

Jadual 1 Formula struktur kompleks

Kompleks	Formula Struktur
1	$K_2[Cu_2(p-OC_6H_4COO)_2(CH_3(CH_2)_{14}COO)_2(p-HOC_6H_4COOH)_2].2H_2O$
2	$[Cu_2(p-HOC_6H_4COO)_2(CH_3(CH_2)_{14}COO)_2(CH_3(CH_2)_{14}COOH)(H_2O)].CH_3CH_2OH$
3	$[Cu_2(p-H_2NC_6H_4COO)_2(CH_3(CH_2)_{14}COO)_2].2H_2O$
4	$K[Cu_2(p-OC_6H_4COO)(CH_3(CH_2)_{14}COO)_3]$
5	$[Cu_2(p-HOC_6H_4COO)(CH_3(CH_2)_{14}COO)_3(CH_3CH_2OH)_2]$
6	$[Cu_2(p-HOC_6H_4COO)(CH_3(CH_2)_{10}COO)_3].H_2O$
7	$[Cu_2(p-HOC_6H_4COO)(CH_3(CH_2)_8COO)_3].CH_3CH_2OH$
8	$[Cu_2(p-HOC_6H_4COO)(CH_3(CH_2)_6COO)_3(CH_3(CH_2)_6COOH)(CH_3CH_2OH)].H_2O$
9	$[Cu_2(CH_3(CH_2)_{14}COO)_2(OH)_2(H_2O)_4].2C_2H_5OH$
10	$K_2[Cu_2(CH_3(CH_2)_{10}COO)_2(OH)_4]$
11	$K_2[Cu_2(CH_3(CH_2)_8COO)_2(OH)_4]$
12	$K_2[Cu_2(CH_3(CH_2)_6COO)_2(OH)_4]$

Formula struktur kompleks dideduksikan daripada analisis unsur, spektroskopi FTIR dan UV-vis. Sifat terma ditentukan melalui TGA dan DSC, manakala sifat mesomorfik ditentukan melalui OPM. Sifat magnet ditentukan melalui kaedah Gouy dengan menggunakan neraca kerentanan magnet, dan sifat redoks melalui voltametri siklik. Seterusnya, GCMS digunakan untuk menganalisis hasil yang terbentuk daripada tindak balas pembentukan ikatan karbon-karbon yang melibatkan metilkarbonil (3,3-dimetil-2-butanon).

Struktur kebanyakan kompleks di atas adalah dimerik '*paddle-wheel*' dengan sama ada geometri empat sisi sama sesatah atau piramid pada pusat kuprum(II).

Kompleks 1 mempunyai kestabilan terma yang paling tinggi ($T_{urai} = 424^{\circ}\text{C}$) berbanding kompleks-kompleks yang lain ($T_{urai} = 200^{\circ}\text{C} - 250^{\circ}\text{C}$). Selanjutnya, kompleks dengan nisbah ligan alkilkarboksilat yang lebih tinggi (aromatik: alifatik = 1:3) adalah lebih stabil secara terma; kestabilan meningkat dengan penambahan dalam panjang rantai alkil. Bagaimanapun, tren berlawanan diperhatikan bagi suhu lebur: kompleks dengan nisbah ligan alkilkarboksilat yang lebih tinggi mempunyai takat lebur yang lebih rendah.

Enam daripada kompleks tersebut (**Kompleks 2, Kompleks 5 - 9**) menunjukkan sifat metalomesogenik. Bagaimanapun, jenis mesofasa tidak dapat dideduksikan dengan jelas daripada OPM.

Semua kompleks adalah magnetik pada suhu bilik. Kecuali **Kompleks 1** yang menunjukkan saling tindakan feromagnet yang lemah ($\mu_{eff} = 3.12 \text{ B.M.}; 2J = 60 \text{ cm}^{-1}$), kompleks-kompleks yang lain mempunyai kemagnetan ($\mu_{eff} = 1.87 \text{ B.M.} - 2.62 \text{ B.M.}$) yang lebih rendah berbanding nilai spin sahaja untuk dua elektron tak berpasangan ($\mu_{eff} = 2.83 \text{ B.M.}$), dengan saling tindakan antiferomagnet pelbagai kekuatan ($2J = -78 \text{ cm}^{-1}$ hingga -346 cm^{-1}). Kompleks dengan nisbah ligan alkilkarboksilat yang lebih tinggi

mempunyai saling tindakan antiferomagnet yang lebih kuat. Bagaimanapun, perbezaan dalam panjang rantai tidak mempunyai kesan yang ketara pada saling tindakan magnet.

Semua kompleks adalah aktif redoks dan menunjukkan tindak balas elektrokimia kuasi-berbalik bertertib. Keupayaan penurunan awal adalah dalam julat 0.07 – 0.30 V.

Kedua-dua **Kompleks 1** dan **Kompleks 4** ‘memangkin’ tindak balas pembentukan ikatan karbon-karbon yang melibatkan 3,3-dimetil-2-butanon. **Kompleks 4** merupakan ‘mangkin’ yang lebih baik kerana hasil tindak balas adalah lebih tulen dan dalam aমাun yang lebih tinggi.

Penemuan penyelidikan ini telah diterbitkan dalam satu (1) jurnal ISI dan dibentang secara lisan atau poster dalam tiga (3) seminar kebangsaan dan empat (4) seminar antarabangsa (**Appendik 1**).