CHAPTER 5 CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

5.1   Conclusions

Two suitable methods for the synthesis of $K_a[Cu_2(p\text{-}OC_6H_4COO)_a(CH_3(CH_2)_nCOO)_{4\text{-}a}]$

and $[Cu_2(p\text{-}HOC_6H_4COO)_a(CH_3(CH_2)_nCOO)_{4\text{-}a}]$ (where a = 1, 2; n = 14, 10, 8, 6) were

the one-pot and ligand-exchange, but not the carbonate-base-acid.

The   one-pot   method   was   also   suitable   for   the   synthesis   of

$[Cu_2(p\text{-}H_2NC_6H_4COO)_a(CH_3(CH_2)_nCOO)_{4\text{-}a}]$,   while   it   was   not   suitable   for

$Cu_2(p\text{-}H_3NC_6H_4COO)_a(CH_3(CH_2)_nCOO)_{4\text{-}a}]X_a$ (where a = 1, 2; n = 14 and X= Cl,

CF_3SO_3 and CH_3COO). On the other hand, both the ligand-exchange and carbonate-

base-acid reactions were not suitable methods for the preparation of these complexes.

A total of twelve complexes were prepared (**Table 5.1**). The structure of most of

the complexes were dimeric paddle-wheel with either square planar or square pyramidal

geometry.

Table 5.1 The structural formulas of the complexes

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

Complex 1 had the highest thermal stability (T_{dec} = 424°C) compared to the other complexes (T_{dec} = 200°C – 250°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. The opposite trend was noted for the melting temperatures: complexes with a higher ratio of the alkylcarboxylate ligands had a lower melting point. The melting temperature increases with increasing alkyl chain length until it reached a certain length (n=10), where it was then decresed.

Six complexes exhibited metallomesogenic properties, though the type of mesophase cannot be deduced with certainty from OPM. These are **Complex 2,** and **Complexes 5 - 9.**

All complexes were magnetic at room-temperature. Except for **Complex 1** which showed a weak ferromagnetic interaction (μ_{eff} = 3.12 B.M.; $2J$ = 60 cm^{-1}), the other complexes had magnetism (μ_{eff} = 1.87 B.M. - 2.62 B.M.) which were lower than the spin-only value for two unpaired electrons (μ_{eff} = 2.83 B.M.), with variable strength of antiferromagnetic interaction ($2J$ = -78 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 and the functional groups (-OH and -NH$_2$) of the arylcarboxylate ligands, did not have much effect on the magnetic interaction.

All of the complexes were redox-active and showed one electron step-wise reduction of [Cu(II)Cu(II)] [Cu(II)Cu(I)] [Cu(I)Cu(I)]. For complexes with the -OH functional group, the mixed-valence [Cu(II)Cu(I)] formed was partially (a) reduced to [Cu(I)Cu(I)], and (b) dissociated to [Cu(II)] and [Cu(I)] ions. On the other hand, for complexes with the–NH$_2$ functional group, the [Cu(I)Cu(I)] formed disproportionated to Cu metal and Cu^{2+} ion. The redox processes were accompanied by extensive structural reorganisation and thus, a 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 purer and in higher amount. This may be due to the difference in structure of both complexes. **Complex 1** was a square pyramidal while **Complex 4** was a square planar. As such, one of the axial positions of **Complex 1** was unavailable to form bond with the ketone compare to **Complex 4.**

5.2   Suggestions for Future Work

For future works, suitable method for the preparation of cationic complexes, such as metathesis reaction, should be investigated/ studied. The structural formulas should be confirmed by single crystal X-ray-diffraction or other more advanced techniques, such as ESI-MS.

To meet the definition as ionic liquids, the melting temperature must be reduced to $100^{o}C$ or below. This may be achieved by changing the alkylcarboxylate ligands to long unsaturated or branched-chain. As for the arylcarboxylate ligands, considering -OH at different location (*o-* or *m-*), as well as using a different substituted group (-NO$_2$, CH$_3$COO and halogens) or organic cations such as RNH$_3^+$.

The carbon-carbon bond-forming reaction should be further investigated to find the optimum conditions, such as increasing the reflux time and to use a different acidic condition. A better technique to isolate the product should be applied, such as by using column chromatography.

Similar studies should be extended to other copper(II) complexes and other metal(II) complexes, and to other carbonyl compounds.