TABLE OF CONTENTS

ABST	RACT	ii
ABST	RAK	iv
ACKN	NOWLEDGEMENT	vi
TABL	LE OF CONTENTS	vii
LIST	OF FIGURES	xi
LIST	OF TABLES	xviii
LIST	OF SCHEMES	XX
CHAPTER 1 INTRODUCTION		1
CHAPTER 2 THEORY AND LITERATURE REVIEW		4
2.1.	Introduction	4
2.2.	Copper(II) carboxylates	4
2.3.	Cyclam	10
2.4.	Fourier transform infrared spectroscopy	17
2.5.	Electronic spectroscopy	20
2.6.	Magnetic properties	22
2.7.	Thermal properties	24
2.8.	Theoretical concepts	31
Refer	References	

3.1.	Introd	luction	37
3.2.	Materials		
3.3.	. Synthesis		
	3.3.1.	Copper(II)-cyclam-alkylcarboxylates	38
	(a)	$[Cu(C_{10}H_{24}N_4)(H_2O)_2](CH_3(CH_2)_5COO)_2.2H_2O(1)$	38
	(b)	$[Cu(C_{10}H_{24}N_4)(H_2O)_2](CH_3(CH_2)_6COO)_2.7H_2O~(\textbf{2})$	39
	(c)	$[Cu(C_{10}H_{24}N_4)(H_2O)_2](CH_3(CH_2)_8COO)_2.2H_2O~(\textbf{3})$	39
	(d)	$[Cu(C_{10}H_{24}N_4)(H_2O)_2](CH_3(CH_2)_{10}COO)_2.2H_2O~(\textbf{4})$	40
	(e)	$[Cu(C_{10}H_{24}N_4)(H_2O)_2](CH_3(CH_2)_{12}COO)_2.2H_2O~(\textbf{5})$	40
	(f)	$[Cu(C_{10}H_{24}N_4)(H_2O)_2](CH_3(CH_2)_{14}COO)_2.2H_2O~(\textbf{6})$	40
	(g)	$\label{eq:cucharge} \begin{split} & [Cu(C_{10}H_{24}N_4)(H_2O)_2](CH_3(CH_2)_7CH((CH_2)_5CH_3)COO)_2. \\ & 5CH_3CH_2OH~(\textbf{7}) \end{split}$	40
	3.3.2.	Copper(II)-cyclam-arylcarboxylates	41
	(a)	$[Cu(p-H_2NC_6H_4COO)_2(C_{10}H_{24}N_4)].2H_2O(8)$	41
	(b)	$[Cu(p-HOC_6H_4COO)_2(C_{10}H_{24}N_4)]$ (9)	41
	(c)	$[Cu(C_{10}H_{24}N_4)(H_2O)_2](p-CH_3OC_6H_4COO)_2.2H_2O (10)$	41
	(d)	$[Cu(C_{10}H_{24}N_4)(H_2O)_2](p-CH_3C_6H_4COO)_2.H_2O(11)$	42
	(e)	$[Cu(p-N \equiv CC_{6}H_{4}COO)(C_{10}H_{24}N_{4})(H_{2}O)] - (p-N \equiv CC_{6}H_{4}COO).3H_{2}O (12)$	42
	(f)	$[Cu(C_{10}H_{24}N_4)(H_2O)_2](C_6H_5COO)_2.2H_2O\ \textbf{(13)}$	42
	(g)	$[Cu(C_{10}H_{24}N_4)(H_2O)_2](C_6F_5COO)_2.2H_2O\ (\textbf{14})$	42
3.4.	Instru	mental analyses	43
	3.4.1.	X-ray crystallographic data and structural determination	43
	3.4.2.	Elemental analyses	43
	3.4.3.	Fourier transform infrared spectroscopy	44
	3.4.4.	Ultraviolet-visible spectroscopy	44

	3.4.5.	Magnetic susceptibility	44
	3.4.6.	Thermogravimetry	45
	3.4.7.	Differential scanning calorimetry	45
	3.4.8.	Optical polarizing microscopy	45
3.5.	Comp	utational methods	46
Refe	erences		46
CHA	APTER	4 RESULTS AND DISCUSSIONS	47
4.1.	Introd	luction	47
4.2.	Coppe	er(II)-cyclam-alkylcarboxylate complexes	47
	4.2.1.	Structural elucidation	47
	(a)	$[Cu(C_{10}H_{24}N_4)(H_2O)_2](CH_3(CH_2)_5COO)_2.2H_2O\ (1)$	47
	(b)	$[Cu(C_{10}H_{24}N_4)(H_2O)_2](CH_3(CH_2)_6COO)_2.7H_2O\left(\textbf{2}\right)$	52
	(c)	$[Cu(C_{10}H_{24}N_4)(H_2O)_2](CH_3(CH_2)_8COO)_2.2H_2O~(\textbf{3})$	55
	(d)	$[Cu(C_{10}H_{24}N_4)(H_2O)_2](CH_3(CH_2)_{10}COO)_2.2H_2O~\textbf{(4)}$	58
	(e)	$[Cu(C_{10}H_{24}N_4)(H_2O)_2](CH_3(CH_2)_{12}COO)_2.2H_2O~(\textbf{5})$	61
	(f)	$[Cu(C_{10}H_{24}N_4)(H_2O)_2](CH_3(CH_2)_{14}COO)_2.2H_2O~(\pmb{6})$	63
	(g)	$\label{eq:cucharge} \begin{split} & [Cu(C_{10}H_{24}N_4)(H_2O)_2](CH_3(CH_2)_7CH((CH_2)_5CH_3)COO)_2. \\ & 5CH_3CH_2OH~(\textbf{7}) \end{split}$	66
	4.2.2.	Physical and chemical properties	70
	(a)	Magnetic studies	70
	(b)	Thermal properties	73
	4.2.3.	Concluding remarks	81
4.3.	Coppe	er(II)-cyclam-arylcarboxylates	81
	4.3.1.	Structural elucidation	81
	(a)	[Cu(<i>p</i> -H ₂ NC ₆ H ₄ COO) ₂ (C ₁₀ H ₂₄ N ₄)].2H ₂ O (8)	81
	(b)	$[Cu(p-HOC_6H_4COO)_2(C_{10}H_{24}N_4)]$ (9)	85

	(c)	$[Cu(C_{10}H_{24}N_4)(H_2O)_2](p-CH_3OC_6H_4COO)_2(10)$	88
	(d)	$[Cu(C_{10}H_{24}N_4)(H_2O)_2](p-CH_3C_6H_4COO)_2.H_2O (11)$	92
	(e)	$[Cu(p-N \equiv CC_{6}H_{4}COO)(C_{10}H_{24}N_{4})(H_{2}O)]$ (p-N \equiv CC_{6}H_{4}COO).3H_{2}O (12)	95
	(f)	$[Cu(C_{10}H_{24}N_4)(H_2O)_2](C_6H_5COO)_2.2H_2O\ \textbf{(13)}$	97
	(g)	$[Cu(C_{10}H_{24}N_4)(H_2O)_2](C_6F_5COO)_2.2H_2O\ (\textbf{14})$	99
	4.3.2.	Physical properties	104
	(a)	Magnetic studies	104
	(b)	Thermal properties	105
	4.3.3.	Concluding remarks	107
4.4.	Molec	ular modelling	108
	4.4.1.	Computational results	109
	(a)	$[Cu(p-H_2NC_6H_4COO)_2(C_{10}H_{24}N_4)].2H_2O(1)$	109
	(b)	$[Cu(p-H_2NC_6H_4COO)_2(C_{10}H_{24}N_4)].2H_2O(\textbf{8})$	114
	(c)	$[Cu(p-HOC_6H_4COO)_2(C_{10}H_{24}N_4)]$ (9)	117
	(d)	$[Cu(C_{10}H_{24}N_4)(H_2O)_2](p\text{-}CH_3OC_6H_4COO)_2(\textbf{10})$	120
	4.4.2.	Concluding remarks	123
Refe	erences		124
CHA	APTER	5 CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK	126
5	5.1. Cor	nclusions	126
5	5.2. Sug	gestions for future work	128
Refe	erences		129

APPENDICES

LIST OF FIGURES

Figure 1.1	The structural formula of cyclam	1
Figure 2.1	The structural formula of cyclam	4
Figure 2.2	Schematic view of the typical paddle-wheel structure of $[Cu_2(RCOO)_4(L)_2]$; L is most often solvent molecules	6
Figure 2.3	An oligomeric structure of $[Cu_2(RCOO)_4]$, showing only two dimers	6
Figure 2.4	Crystal structure of copper(II) decanoate, [Cu ₂ (CH ₃ (CH ₂) ₈ COO) ₄]; hydrogen atoms were not shown	7
Figure 2.5	ORTEP view of the structure $[Cu(CH_3(CH_2)_7COO)_2(py)_2(H_2O)]$ with atom labelling scheme, hydrogen atoms were not drawn	8
Figure 2.6	(a) ORTEP view of $[Cu(CH_3(CH_2)_8COO)_2(NH_3)_2]$.H ₂ O with atom labelling scheme, hydrogen atoms were omitted; and (b) schematic presentation of the coordination environment around the copper atom	8
Figure 2.7	Crystal structure of [Cu ₂ (o-NO ₂ C ₆ H ₄ COO) ₄ (CH ₃ CN) ₂]	9
Figure 2.8	Crystal structure of [Cu ₂ (<i>o</i> -FC ₆ H ₄ COO) ₄ (CH ₃ OH) ₂]	9
Figure 2.9	Crystal structure of $[Cu_2(CF_3(CH_2)_3COO]_4$, showing two paddlewheel structures	10
Figure 2.10	The schematic representation of cyclam	10
Figure 2.11	(a) Schematic representations of the five possible cyclam configurations according to Bosnich's nomenclature; wedge refers to an N–H bond pointing above the plane and hashed wedge is an N–H bond that points below; and (b) idealized structures of the octahedral complexes of cyclam	12
Figure 2.12	Molecular structure of [Zn(cyclam)(cis-OOCCH=CHCOO)] with atom-labelling scheme; carboxylate groups are directly coordinated to zinc(II) ion	13
Figure 2.13	Molecular view of [Zn(cyclam)(H ₂ O) ₂](<i>trans</i> -OOCCH=CHCOO) with atom-labelling scheme; fumarate anion is not coordinated to Zn atom	14
Figure 2.14	Molecular structure of $[Ni(cyclam)(H_2O)_2]$ -(<i>trans</i> -OOCHC=CHCOO). 4H ₂ O; Ni(II) ion in the cyclam is six-coordinated with distorted octahedral geometry with four <i>aza</i> -N atoms in the equatorial plane and water molecules in the apices	15
Figure 2.15	Molecular structure of $[Ni(cyclam)(C_6H_5COO)_2]$, showing direct coordination between Ni atom and carboxylate groups	16

Figure 2.16	Molecular structure of [Cu(cyclam)(H ₂ O) ₂](C ₆ H ₅ COO) ₂ .2H ₂ O	17
Figure 2.17	Molecular structure of [Cu(cyclam)(H ₂ O) ₂](C ₆ F ₅ COO) ₂ .2H ₂ O	17
Figure 2.18	An infrared spectrum showing the position of COO stretching band	19
Figure 2.19	(a) The UV-vis spectrum of copper(II) acetate, $[Cu_2(CH_3COO)_4(H_2O)_2]$; and (b) the schematic view of the structure of the complex	21
Figure 2.20	Schematic representation of a Gouy balance	23
Figure 2.21	TG/DTA curves of [Cu ₂ (CH ₃)(CH ₂) ₁₆ COO) ₄]	24
Figure 2.22	DSC curves of $[Cu_2(CH_3)(CH_2)_nCOO)_4]$ (<i>n</i> = 10, 12, 14 and 16)	25
Figure 2.23	Representative examples of: (a) calamitic; and (b) discotic mesogens	27
Figure 2.24	Schematic representations of: (a) calamitic mesogen; and (b) discotic mesogen. Arrows indicate the axes of the molecules that align to the director n	27
Figure 2.25	(a) Schematic representation; and (b) schlieren texture of a nematic mesophase	28
Figure 2.26	Schematic representations of smectic phases, showing layered structure: (a) SmA; and (b) SmC (tilted)	28
Figure 2.27	2-Alkoxy-5-phenylpyrimidines	29
Figure 2.28	SmA mesophase of 2-Alkoxy-5-phenylpyrimidines ($n = 5$), displaying a fan-shaped texture under crossed polarizers upon cooling from the isotropic liquid	29
Figure 2.29	DSC curve of 2-Alkoxy-5-phenylpyrimidines ($n = 6$)	30
Figure 2.30	Mesogenic dimer bearing hydrazide group	30
Figure 2.31	A distinct difference between: (a) SmA (focal conic texture); and (b) SmC (fan-shaped texture). The red arrows indicate the direction of the polarisers	31
Figure 2.32	An optical texture of (a) N_D [48]; and (b) Col_h	31
Figure 2.33	FTIR spectra of 2-chloro-4-nitroaniline: (a) calculated and (b) observed	32
Figure 2.34	Molecular electrostatic potential surface of 6-nitro-m-toluic acid	33

Figure 3.1	The structural formula of cyclam	37
Figure 4.1	Molecular structure of 1 , showing displacement ellipsoids at 50% probability level; operator used to generate symmetry equivalent elements: x , $\frac{1}{2}$ - y , $-\frac{1}{2}$ + z	48
Figure 4.2	Representation of the chair conformation of the six-membered (A) and gauche five-membered chelate ring (B) of cyclam group of 1 ; carbon bound H-atoms were not shown	49
Figure 4.3	Unit cell of 1, viewed along crystallographic b-axis, N–H···O and O–H···O bond is indicated as green and pink dashes respectively (some hydrogen atoms were not shown)	49
Figure 4.4	Molecular view of the dimeric paddlewheel structure of $[Cu_2(CH_3(CH_2)_5COO)]_4$, drawn at 70% probability level; symmetry elements are related by operator $-x$, $2-y$, $-z$	50
Figure 4.5	The FTIR spectrum of 1	51
Figure 4.6	The UV-vis spectrum of 1	52
Figure 4.7	The FTIR spectrum of 2	53
Figure 4.8	The UV-vis spectrum of 2	54
Figure 4.9	Schematic representation of the proposed structure of 2 ; N–H···O and O–H···O bond is indicated as green and pink dashes respectively; the remaining five solvated H_2O molecules are not shown	55
Figure 4.10	Molecular structures of 3 , showing displacement ellipsoids at 70% probability level; operator used to generate symmetry equivalent elements: $1-x$, $1-y$, $1-z$	56
Figure 4.11	Unit cell of 3 , viewed along crystallographic <i>b</i> -axis, N–H···O and O–H···O bond is indicated as green and pink dashes respectively (some hydrogen atoms were not shown)	56
Figure 4.12	The FTIR spectrum of 3	57
Figure 4.13	The UV-vis spectrum of 3	58
Figure 4.14	Molecular structures of 4 , showing displacement ellipsoids at 70% probability level; operator used to generate symmetry equivalent elements: $2-x$, $-y$, $2-z$	59
Figure 4.15	Unit cell of 4 , viewed along crystallographic <i>b</i> -axis, N–H···O and O–H···O bond is indicated as green and pink dashes respectively (some hydrogen atoms were not shown)	59
Figure 4.16	The FTIR spectrum of 4	60

Figure 4.17	The UV-vis spectrum of 4	60
Figure 4.18	Molecular structures of 5 , showing displacement ellipsoids at 70% probability level; operator used to generate symmetry equivalent elements (unlabelled atoms): $2-x$, $-y$, $-z$	61
Figure 4.19	Unit cell of 5, viewed along crystallographic <i>b</i> -axis, N–H····O and O–H····O bond is indicated as green and pink dashes respectively (some hydrogen atoms were not shown)	62
Figure 4.20	The FTIR spectrum of 5	62
Figure 4.21	The UV-vis spectrum of 5	63
Figure 4.22	Molecular structures of 6 , showing displacement ellipsoids at 50% probability level; operator used to generate symmetry equivalent elements: $-x$, $-y$, $1-z$	64
Figure 4.23	Unit cell of 6 , viewed along crystallographic b-axis, N–H····O and O–H····O bond is indicated as green and pink dashes respectively (some hydrogen atoms were not shown)	64
Figure 4.24	The FTIR spectrum of 6	65
Figure 4.25	The UV-vis spectrum of 6	65
Figure 4.26	The FTIR spectrum of 7	66
Figure 4.27	The UV-vis spectrum of 7	67
Figure 4.28	Schematic representation of the proposed structure of 7 ; N–H···O and O–H···O bond is indicated as green and pink dashes respectively; the five solvated CH_3CH_2OH molecules are not shown	68
Figure 4.29	The extended hydrogen-bond network of 1 viewed down the <i>a</i> -axis, yellow dashed lines indicate $N-H\cdots O$ bond and blue dashed lines indicate $O-H\cdots O$ bond; the $CH_3(CH_2)_5COO^-$ chains were shortened and lattice H_2O molecules were omitted for clarity.	72
Figure 4.30	The extended hydrogen-bond network of 6 viewed down the <i>b</i> -axis, yellow dashed lines indicate N–H···O bond and blue dashed lines indicate O–H···O bond; the $CH_3(CH_2)_{14}COO^-$ chains were shortened.	73

Figure 4.31 TGA trace of **1**

74

Figure 4.32	DSC traces of 1	75
Figure 4.33	Photomicrographs of 1 under crossed polarizers (a) melting at 44.2 °C; (b) clearing to an isotropic liquid at 135.0 °C; (c) and (d) crystals at two different sites upon cooling to room temperature	76
Figure 4.34	TGA trace of 6	77
Figure 4.35	DSC traces of 6	77
Figure 4.36	DSC traces of 6 separated to: (a) first cycle; and (b) second cycle	78
Figure 4.37	Photomicrographs of 6 under crossed polarizers on cooling at: (a) 102 °C; (b-d) 88 °C at three different sites; (e) crystalizing from left to right at 56.9 °C; and (f) room temperature	80
Figure 4.38	Molecular structure of 8 , showing displacement ellipsoids at 70% probability level; operator used to generate symmetry equivalent elements (unlabelled atoms): $-x$, $2-y$, $-z$	82
Figure 4.39	Unit cell of 8, viewed along crystallographic <i>a</i> -axis; the crystal structure formed two dimensional networks via O–H···O and N–H···O hydrogen bond (pink and green dashed lines, respectively).	83
Figure 4.40	The FTIR spectrum of 8	84
Figure 4.41	The UV-vis spectrum of 8	85
Figure 4.42	Molecular structure of 9 , showing displacement ellipsoids at 70% probability level; operator used to generate symmetry equivalent elements (unlabelled atoms): $1-x$, $1-y$, $-z$	86
Figure 4.43	Unit cell of 9 , viewed along crystallographic <i>c</i> -axis; the crystal structure formed two dimensional networks via O–H···O and N–H···O hydrogen bond (pink and green dashed lines, respectively).	87
Figure 4.44	The FTIR spectrum of 9	87
Figure 4.45	The UV-vis spectrum of 9	88
Figure 4.46	Molecular structure of 10 , showing displacement ellipsoids at 70% probability level; operator used to generate symmetry equivalent elements (unlabelled atoms): $1-x$, $1-y$, $2-z$	89
Figure 4.47	Unit cell of 10 , viewed along the <i>a</i> -axis; the O–H···O and N–H···O hydrogen bonds (pink and green dashed lines, respectively) have led to the formation of chain along the <i>b</i> -axis.	90

Figure 4.48	The FTIR spectrum of 10	91
Figure 4.49	The UV-vis spectrum of 10	91
Figure 4.50	Molecular structure of 11 , showing displacement ellipsoids at 70% probability level	92
Figure 4.51	Unit cell of 11 , viewed along the <i>c</i> -axis; the O–H···O and N–H···O hydrogen bonds (pink and green dashed lines, respectively) have led to the formation chain along the <i>b</i> -axis.	93
Figure 4.52	The FTIR spectrum of 11	94
Figure 4.53	The UV-vis spectrum of 11	94
Figure 4.54	The molecular structure of 12 , showing displacement ellipsoids at 70% probability level	95
Figure 4.55	The FTIR spectrum of 12	96
Figure 4.56	The UV-vis spectrum of 12	97
Figure 4.57	Molecular structure of 13, showing displacement ellipsoids at 70% probability level; operator used to generate symmetry equivalent elements (unlabelled atoms): $-1-x$, $-1-y$, $-z$	98
Figure 4.58	The FTIR spectrum of 13	98
Figure 4.59	The UV-vis spectrum of 13	99
Figure 4.60	Molecular structure of 14 , showing displacement ellipsoids at 70% probability level; operator used to generate symmetry equivalent elements (unlabelled atoms): $1-x$, $1-y$, $1-z$	100
Figure 4.61	Unit cell of 14 , viewed along the <i>c</i> -axis; the O–H…O and N–H…O hydrogen bonds (pink and green dashed lines, respectively) have led to the formation chain along the <i>a</i> -axis.	101
Figure 4.62	The FTIR spectrum of 14	102
Figure 4.63	The UV-vis spectrum of 14	102
Figure 4.64	TGA trace of 9	106

Figure 4.65	TGA trace of 10	106
Figure 4.66	TGA trace of 12	107
Figure 4.67	The optimized structure of 1	109
Figure 4.68	Comparison of theoretical and experimental FTIR spectra of 1	111
Figure 4.69	Colour scheme showing relative electrostatic charge distribution	112
Figure 4.70	Molecular electrostatic potential map surface map of 1	113
Figure 4.71	The optimized structure of 8	114
Figure 4.72	Comparison of theoretical and experimental FTIR spectra of 8	115
Figure 4.73	The molecular electrostatic potential surface map of 8	117
Figure 4.74	The optimized structure of 9	118
Figure 4.75	Comparison of theoretical and experimental FTIR spectra of 9	119
Figure 4.76	The molecular electrostatic potential surface map of 9	120
Figure 4.77	The optimized structure of 10	121
Figure 4.78	Comparison of theoretical and experimental FTIR spectra of 10	122
Figure 4.79	The molecular electrostatic potential surface map of 10	123

LIST OF TABLES

Table 1.0	Structural formulas of complexes	ii
Jadual 1.0	Formula struktur kompleks	iv
Table 2.1	Relative energies calculated for the five isomers of cyclam	11
Table 2.2	Wavenumbers of COO ⁻ stretches of Zn(II) complexes with different binding mode	20
Table 2.3	Temperature of phase transitions from solid to liquid crystal mesophase from DTA and DSC, and enthalpy values of the selected copper(II) alkylcarboxylates	25
Table 3.1	The chemicals used in the project, arranged in alphabetical order	38
Table 4.1	FTIR data and assignments of 1	51
Table 4.2	Elemental analytical data of 2	52
Table 4.3	Elemental analytical data of 7	66
Table 4.4	Selected crystal parameters and refinement details of aliphatic crystalline complexes	69
Table 4.5	Distance values between the Cu atom and its ligand	70
Table 4.6	The magnetic data for 1 and 6	71
Table 4.7	DSC data of 6	79
Table 4.8	The FTIR and assignments of 8	84
Table 4.9	Selected crystal parameters and refinement details of aromatic crystalline complexes	103
Table 4.10	The magnetic data for 9, 10 and 12	105
Table 4.11	Comparison of selected theoretical and experimental bond lengths of 1 1	10

Table 4.12	The partial charge energy for selected atoms of 1	111
Table 4.13	Comparison of selected theoretical and experimental bond lengths of 8	115
Table 4.14	The partial charge energy for selected atoms of 8	116
Table 4.15	Comparison of selected theoretical and experimental bond length of ${\bf 8}$	118
Table 4.16	The partial charge energy for selected atoms of 9	119
Table 4.17	Comparison of selected theoretical and experimental bond lengths of 10	121
Table 4.18	The partial charge energy for selected atoms of 10	122
Table 5.1	Chemical formula of copper(II) alkylcarboxylate-cyclam complex	126
Table 5.2	Chemical formula of copper(II) arylcarboxylate-cyclam complex	127

LIST OF SCHEMES

Scheme 2.1	Reaction equations for the formation of $[Cu_2(RCOO)_4]$	5
Scheme 2.2	Different binding mode of carboxylate ion	18