

Contents

	Page
บทคัดย่อ	(3)
Abstract(English)	(5)
Acknowledgment	(7)
The relevancy of the research work to Thailand	(9)
Contents	(11)
List of tables	(13)
List of figures	(15)
Lists of abbreviations	(18)
Chapter	
1) Introduction	1
1.1 Introduction	1
1.2 Literature reviews	5
1.3 Objectives	12
2) Method of study	14
2.1 Chemicals	14
2.2 Instruments	14
2.3 Preparation of copper(I) complexes	15
2.4 Methods for Determination	16
2.4.1 X-ray Fluorescence Spectrometry	16
2.4.2 Fourier Transform Infrared Spectroscopy	16
2.4.3 Elemental Analysis	16
	(11)

Contents (continued)

	Page
2.4.4 Single crystal X-ray diffraction	16
3) Results	30
3.1 Preparation of copper(I) complexes	30
3.2 X-ray Fluorescence Spectrometry	31
3.3 Fourier Transform Infrared Spectroscopy	31
3.4 Elemental Analysis	31
3.5 Single crystal X-ray diffraction	47
4) Discussion	97
4.1 Preparation of copper(I) complexes	97
4.2 X-ray fluorescence spectrometry	98
4.3 Elemental Analysis	98
4.4 Fourier Transform Infrared spectroscopy	98
4.5 Single crystal X-ray diffraction	105
5) Conclusion	114
6) Bibliography	116
Appendix	124
Appendix A	125
Appendix B	128
Vitae	152

List of tables

Table		Page
1	Copper(I) Thiourea and substituted Thiourea complexes	13
2	The suitable conditions of synthesis complexes	30
3	The physical properties of ligands and compounds	30
4	The partial elemental analyses of compound	31
5	Crystallographic data for [Cu(ptu) ₄]Cl	47
6	Non-hydrogen interatomic distances of [Cu(ptu) ₄]Cl	48
7	Non-hydrogen interatomic angles of [Cu(ptu) ₄]Cl	49
8	Crystallographic data for [Cu ₄ (ptu) ₆ Br ₄] ₂	53
9	Non-hydrogen interatomic distances of [Cu ₄ (ptu) ₆ Br ₄] ₂	54
10	Non-hydrogen interatomic angles of [Cu ₄ (ptu) ₆ Br ₄] ₂	63
11	Crystallographic data for [Cu ₄ (ptu) ₆ I ₄] ₂	74
12	Non-hydrogen interatomic distances of [Cu ₄ (ptu) ₆ I ₄] ₂	75
13	Non-hydrogen interatomic angles of [Cu ₄ (ptu) ₆ I ₄] ₂	82
14	The infrared spectra of the ligands ptu and the studied compounds	106
15	The selected bond distances of the studied compounds	113
16	The selected bond angles of the studied compounds	113
17	Non-hydrogen atom coordinates and isotropic thermal parameters of [Cu(ptu) ₄]Cl	128
18	Hydrogen atom coordinates and isotropic thermal parameters of [Cu(ptu) ₄]Cl	128
19	Non-hydrogen thermal parameters of [Cu(ptu) ₄]Cl	129

Lists of tables (continued)

Table		Page
20	Non-hydrogen atom coordinates and isotropic thermal parameters of [Cu ₄ (ptu) ₆ Br ₄]	130
21	Hydrogen atom coordinates and isotropic thermal parameters of [Cu ₄ (ptu) ₆ Br ₄]	134
22	Non-hydrogen thermal parameters of [Cu ₄ (ptu) ₆ Br ₄]	137
23	Non-hydrogen atom coordinates and isotropic thermal parameters of [Cu ₄ (ptu) ₆ I ₄]	141
24	Hydrogen atom coordinates and isotropic thermal parameters of [Cu ₄ (ptu) ₆ I ₄]	145
25	Non-hydrogen thermal parameters of [Cu ₄ (ptu) ₆ Br ₄]	148

List of figures

Figure		Page
1	(a) The structure of thiourea	2
	(b) The structure of <i>N</i> -phenylthiourea (ptu)	2
2	The tautomerism structure of Thiourea	3
3	An ORTEP drawings of the $\text{Cu}_4[\text{SC}(\text{NH}_2)_2]_6^{4+}$ (a) and $\text{Cu}_4[\text{SC}(\text{NH}_2)_2]_9^{4+}$ (b) molecular ions with emphasis on the Cu_4S_6 central polyhedron	7
4	The two cations of $[\text{Cu}(\text{etu})_3]_2\text{SO}_4$ projected (a) normal to (b) down the three fold axis (normal to the S_3 plane)	8
5	Molecular configuration and numbering scheme for $[\text{Cu}_4(\text{tu})_7]\text{SO}_4 \cdot \text{H}_2\text{O}$	9
6	The structure of $[\text{Cu}_4\text{I}_4(\text{C}_3\text{H}_8\text{N}_2\text{S})_6] \cdot \text{H}_2\text{O}$	10
7	Molecular structure of the chiral complex $\Lambda[\text{CuCl}(\text{HL}_2)_3]$	11
8	A flowchart for the steps involved in a crystal structure determination	17
9	Crystal mounting	19
10	The Weissenberg camera	20
11	The SMART APEX CCD X-ray diffractometer	22
12	A 3-axis goniometer	23
13	Goniometer head adjustment locations	24
14	Crystal center on crosshairs ($\phi = 90^\circ$)	24
15	Image frame following 60-second rotation	25
16	The X-ray fluorescence spectrum of $[\text{Cu}(\text{ptu})_4]\text{Cl}$ (Cu atom)	33
17	The X-ray fluorescence spectrum of $[\text{Cu}(\text{ptu})_4]\text{Cl}$ (Cl atom)	34
18	The X-ray fluorescence spectrum of $[\text{Cu}(\text{ptu})_4]\text{Cl}$ (S atom)	35

List of figures (continued)

Figure		Page
19	The X-ray fluorescence spectrum of $[\text{Cu}_4(\text{ptu})_6\text{Br}_4]$ (Cu atom)	36
20	The X-ray fluorescence spectrum of $[\text{Cu}_4(\text{ptu})_6\text{Br}_4]$ (Br atom)	37
21	The X-ray fluorescence spectrum of $[\text{Cu}_4(\text{ptu})_6\text{Br}_4]$ (S atom)	38
22	The X-ray fluorescence spectrum of $[\text{Cu}_4(\text{ptu})_6\text{I}_4]$ (Cu atom)	39
23	The X-ray fluorescence spectrum of $[\text{Cu}_4(\text{ptu})_6\text{I}_4]$ (I atom)	40
24	The X-ray fluorescence spectrum of $[\text{Cu}_4(\text{ptu})_6\text{I}_4]$ (S atom)	41
25	The infrared spectrum of ligand <i>N</i> -phenylthiourea	42
26	The infrared spectrum of $[\text{Cu}(\text{ptu})_4]\text{Cl}$	43
27	The infrared spectrum of $[\text{Cu}_4(\text{ptu})_6\text{Br}_4]$	44
28	The infrared spectrum of $[\text{Cu}_4(\text{ptu})_6\text{I}_4]$	45
29	The oscillation photograph of $[\text{Cu}_4(\text{ptu})_6\text{I}_4]$	46
30	The zero layer Weissenberg photograph of $[\text{Cu}_4(\text{ptu})_6\text{I}_4]$	46
31	The structure of $[\text{Cu}(\text{ptu})_4]\text{Cl}$ (H atoms omitted for clarity)	50
32	Unit cell contents of $[\text{Cu}(\text{ptu})_4]\text{Cl}$ projected down <i>c</i>	51
33	Unit cell contents of $[\text{Cu}(\text{ptu})_4]\text{Cl}$ projected down <i>a</i>	52
34	The structure of $[\text{Cu}_4(\text{ptu})_6\text{Br}_4]_2$ (H atoms omitted for clarity)	71
35	Unit cell contents of $[\text{Cu}_4(\text{ptu})_6\text{Br}_4]_2$ projected down <i>c</i>	72
36	Unit cell contents of $[\text{Cu}_4(\text{ptu})_6\text{Br}_4]_2$ projected down <i>a</i>	73
37	The structure of $[\text{Cu}_4(\text{ptu})_6\text{I}_4]_2$ (H atoms omitted for clarity)	93
38	The core structure of $[\text{Cu}_4(\text{ptu})_6\text{I}_4]$ (H, C and N atoms omitted for clarity)	94

List of figures (continued)

Figure		Page
39	Unit cell contents of $[\text{Cu}_4(\text{ptu})_6\text{I}_4]_2$ projected down a	95
40	Unit cell contents of $[\text{Cu}_4(\text{ptu})_6\text{I}_4]_2$ projected down c	96
41	A projection of $[\text{Cu}(\text{ptu})_4]^+$ down the $\bar{4}$ axis	109
42	The cation of $[\text{Cu}(\text{ptu})_4]^+$	109
43	(a)The dimeric structure of molecule A of $\text{Cu}_2(\text{ptu})_4\text{Cl}_2$	110
	(b)The dimeric structure of molecule B of $\text{Cu}_2(\text{ptu})_4\text{Cl}_2$	110
44	The two independent molecules of (a) $[\text{Cu}_4(\text{ptu})_6\text{Br}_4]_2$ and $[\text{Cu}_4(\text{ptu})_6\text{I}_4]_2$	112
45	The Bravais lattices	126
46	Showing the cell parameters (a , b , c , α , β and γ) of some the Bravais lattice	127

List of abbreviations

°	=	degree
Å	=	Angstrom unit (1 Å = 1 ⁻¹⁰ metre)
A.R.	=	Analytical Reagent
L.R.	=	Lab Reagent
cm ⁻¹	=	wave number
D_c	=	calculated density
D_m	=	measured density
g	=	gram
kg	=	kilogram
g/cm ³	=	gram per cubic centimeter
h	=	hour
K	=	Kelvin
keV	=	kilo electron volt
mL	=	milliliter
mm	=	millimeter
mmol	=	millimole
ptu	=	<i>N</i> -phenylthiourea