

Contents

	Page
Contents	vi
List of Tables	viii
List of Figures	x
List of Abbreviations and Symbols	xii
Chapter 1 Introduction	1
Introduction	1
Literature reviews	11
Objectives	20
Chapter 2 Materials and methods	21
Materials	21
Instruments	22
Syntheses of complexes	23
Chapter 3 Results	26
Syntheses of complexes	26
Products characterizations	34
X-ray fluorescence spectrometry	35
Single crystal X-ray diffraction	41
Infrared spectrometry	59
Chapter 4 Discussions	71
Syntheses of complexes	71
Products characterizations	73
X-ray fluorescence spectrometry	73
Single crystal X-ray diffraction	74
Infrared spectrometry	75
Chapter 5 Conclusions	83

Contents (Continued)

	Page
References	84
Vitae	89

List of Tables

Table	Page
1 Comparative solubility of curcumin in various solvents	26
2 Results from 2.3.2 (method 1), curcumin dissolved in MeOH	27
3 Results from 2.3.2 (method 1), curcumin dissolved in acetone)	27
4 Results from 2.3.2 (method 2.1)	28
5 Results from 2.3.2 (method 2.2)	28
6 Results from 2.3.2 (method 2.3)	29
7 Physical appearance of complexes	30
8 Physical appearance of crystals at various concentration of NaOH	31
9 Products obtained from the reactions when adding lanthanide ions	32
10 Products obtained from the reactions when adding dilute (5 folds) lanthanide ions	33
11 Crystal data for CULa (Curcumin + La(III))	43
12 Crystal data for CUCr (Curcumin + Cr(III))	43
13 Crystal data for B2	44
14 Crystal data and structure refinement for A1	45
15 Atomic coordinations ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for A1	48
16 Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for A1	49
17 Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for A1	51
18 Bond lengths [\AA] and angles [$^\circ$] for A1	52
19 Torsion angles [$^\circ$] for A1	57
20 The previous studies of infrared absorption spectra for curcuminoids and some metal curcumin complexes	78

List of Tables (Continued)

Table		Page
21	IR data of curcumin, Fe-CU1 and Fe-CU2	80
22	The vibrational modes of metal curcumin complexes	81

List of Figures

Figure		Page
1	Structures of enol form (1) and diketone (2)	3
2	Numbering of the atoms and the molecular packing in crystals of curcumin	11
3	Geometry in the enol ring and the hydrogen bond system	11
4	Structure of the gold(I) curcumin complex	12
5	Structures of curcumin (1), demethoxycurcumin (2) and bis-demethoxycurcumin (3)	12
6	Structures of vanillin (1), ferulic acid (2), a dimer of curcumin (3)	13
7	Structures of curcumin (1) and curcuminoids (2-9)	15
8	Structures of bis-curcuminoids 3 and 4	16
9	The structure of curcumin and curcumin derivatives	18
10	The structure of the metal complexes	18
11	Structure of the Cu(II)-curcumin complex	19
12	The XRF spectrum of Fe in Fe-CU1	35
13	The XRF spectrum of Fe in Fe-CU2	35
14	The XRF spectrum of Fe, Ni and Cu in La-CU	36
15	The XRF spectrum of Ca and Ti in La-CU	37
16	The XRF spectrum of Si in La-CU	38
17	The XRF spectrum of Al in La-CU	39
18	The XRF spectrum of Mg in La-CU	40
19	The molecular plot of CUCr, CULa, A1, B2 (curcumin)	41
20	Numbering of the atoms and the molecular packing in crystals of A1 (curcumin)	42
21	IR spectrum of curcumin (in-house separation)	59

List of Figures (Continued)

Figure		Page
22	IR spectrum of curcumin (commercial)	59
23	IR spectrum of Fe-CU1	60
24	IR spectrum of Fe-CU2	61
25	IR spectrum of Dy-CU	62
26	IR spectra of Dy-CU and commercial curcumin	62
27	IR spectrum of Gd-CU	63
28	IR spectra of Gd-CU and commercial curcumin	63
29	IR spectrum of Er-CU	64
30	IR spectra of Er-CU and commercial curcumin	64
31	IR spectrum of La-CU	65
32	IR spectra of La-CU and commercial curcumin	65
33	IR spectrum of Nd-CU	66
34	IR spectra of Nd-CU and commercial curcumin	66
35	IR spectrum of Pr-CU	67
36	IR spectra of Pr-CU and commercial curcumin	67
37	IR spectrum of Yb-CU	68
38	IR spectra of Yb-CU and commercial curcumin	68
39	IR spectrum of Sm-CU(0.5)	69
40	IR spectra of Sm-CU(0.5) and commercial curcumin	69
41	IR spectrum of Sm-CU	70
42	IR spectra of Sm-CU and commercial curcumin	70

List of Abbreviations and Symbols

°	=	degree
Å	=	angstrom unit ($1 \text{ Å} = 10^{-10}$ meter)
A.R.	=	Analytical Reagent
cm^{-1}	=	wavenumber
IR	=	Infrared
L	=	ligand
g	=	gram
g/cm^3	=	gram per cubic centimeter
mg	=	milligram
mmol	=	millimole
mL	=	milliliter
keV	=	kilo electron volt

The Relevance of the Research Work to Thailand

Curcumin is a yellow pigment of turmeric, a spice manufactured from the root of *Curcuma longa* which is a member of the *Zingiberaceae* (ginger) family cultivated extensively in India, China, and other countries with a tropical climate, including Thailand. It has been used as herbal medicine since ancient time as well as in flavoring and coloring foods. As herbal medicine, tumeric (curcumin) has been found to have the following effects: antihepatotoxic, antihyperlipidemic, anti-inflammatory, antioxidant, antitumoral, antimicrobial, antifertile, anti-insect, and anti-Alzheimer's disease. Studying metal-curcumin complexation is one interesting research topic and is appropriate for Thailand since *Curcuma longa* can be found in almost every part of the country. It helps link the basic chemistry knowledge to medicinal applications. The interaction between the active ingredient of medicinal plants and metal ions in the body frequently involving complexation and most of them through the process called metal chelation. The molecule of curcumin has a functional group that can form metal chelation and this is probably the key step to explain why curcumin is used as medicine. Knowledge from complex formation between curcumin and several potential toxic metal ions can be used to explain the drug actions and also to develop a new drug based on curcumin as raw material. Through understanding the chemistry of curcumin and metal ions will support and popularize the usage of curcumin as herbal medicine. The widespread usage of curcumin will benefit the *Curcuma longa* farmers and maybe in the future *Curcuma longa* can be added to the economic plants list for Thailand.