



Ain Shams University
Faculty of Education
Chemistry Department

**Synthesis, physicochemical studies and
molecular modeling of metal complexes
of some hydrazones derived from
2-amino-3-formylchromone**

A Thesis Submitted

By

Shery Anwar Fahmy Ibrahim

B.Sc. & Ed. 2007

M.Sc. 2014

For The Degree of Doctor of Philosophy

For the Teacher's Preparation

In Science

(Inorganic Chemistry)

Supervisors

Prof. Dr. Ali Mahmoud Taha

Prof. Dr. Magdy Ahmed Mohamed Ibrahim

Dr. Omima Mohamed Ibrahim

To

Department of Chemistry

Faculty of Education

Ain Shams University

Cairo -2019

—

|



Ain Shams University
Faculty of Education

Synthesis, physicochemical studies and molecular modeling of metal complexes of some hydrazones derived from 2-amino-3-formylchromone

By

Shery Anwar Fahmy Ibrahim

B.Sc. & Ed. (2007)

M.Sc. (2014)

Under the supervision of

1- Prof. Dr. Ali Mahmoud Taha

Prof. of Inorganic Chemistry, Faculty of Education, Ain Shams University.

2- Prof. Dr. Magdy Ahmed Mohamed Ibrahim

Prof. of Organic Chemistry, Faculty of Education, Ain Shams University.

3- Dr. Omima Mohamed Ibrahim Adly

Ass. Prof. of Inorganic Chemistry, Faculty of Education, Ain Shams University.

—

|



Ain Shams University
Faculty of Education

Approval Sheet

"Synthesis, physicochemical studies and molecular modeling of metal complexes of some hydrazones derived from 2-amino-3-formylchromone"

Supervisors

Signature

Prof. Dr. Ali Mahmoud Taha

.....

Prof. of Inorganic Chemistry, Faculty of Education, Ain Shams University.

Prof. Dr. Magdy Ahmed Mohamed

.....

Prof. of Organic Chemistry, Faculty of Education, Ain Shams University.

Dr. Omima Mohamed Ibrahim

.....

Assistant Prof. of Inorganic Chemistry, Faculty of Education, Ain Shams University.

Head of Chemistry Department

Prof. Dr. Mohamed Abass Mohamed

.....

Higher studies:

The thesis was approved

Approval date / / 2019

Approved by Council of Faculty

Approved by Council of

University Date / / 2019

Date / / 2019

—

|

Acknowledgement

*First of all, thanks to **GOD**, for helping me to accomplish this thesis.*

I would like to express deep thanks and gratitude to my professors for their continuous and valuable helping in interpretation of the results and lay out of this thesis:

*Prof. Dr. **Ali Mahmoud Taha**; Prof. of Inorganic Chemistry, Faculty of Education, Ain Shams University.*

*Prof. Dr. **Magdy Ahmed Mohamed**; Prof. of Organic Chemistry, Faculty of Education, Ain Shams University.*

*Dr. **Omima Mohamed Ibrahim**; Assistant Prof. of Inorganic Chemistry, Faculty of Education, Ain Shams University*

*Many thanks to Prof. Dr. **Mohamed Abass Mohamed**; Head of the Department of Chemistry, Faculty of Education, Ain Shams University. Also, Many thanks to Prof. Dr. **Mahmoud Mohamed Mashaly** and Prof. Dr. **Ali Mahmoud Taha**; the previous Head of the Department of Chemistry, Faculty of Education, Ain Shams*

Shery Anwar Fahmy Ibrahim

—

|

Contents

List of Schemes	i
List of Tables	iii
List of Figures	viii
List of diagrams	xiv
List of abbreviations	xv
Abstract	xviii
Aim of the work	xx

Chapter I

INTRODUCTION

(Metal complexes with chromone derivatives)

1.1. Complexes derived from 3-formylchromones	2
1.2. Complexes derived from Schiff bases and hydrazones of 3-formylchromone.	10

Chapter II

EXPERIMENTAL AND THEORETICAL BACKGROUND

(2.1) Materials	46
(2.2) Preparation of organic compounds	46
(2.2.1) Preparation of chromone-3-carboxaldehyde	47
(2.2.2) Preparation of chromone-3-carboxaldehyd-oxime	47
(2.2.3) Preparation of 2-aminochromone-3-carboxaldehyde	47
(2.2.4) Synthesis of hydrazone ligands	48
(2.2.4.1) 2-[(2-Aminochromon-3-yl)methylidene]hydrazinecarboxamide (ACMHC, HL _a)	48
(2.2.4.2) 2-[(2-Aminochromon-3-yl)methylidene]- <i>N</i> -phenylhydrazine carbothioamide (ACMPHC, HL _b)	48
(2.3) Synthesis of copper(II)-hydrazone complexes	50

(2.3.1) General Procedure	50
(2.3.1.1) Synthesis of binary [(L _a)Cu(NO ₃)]·H ₂ O complex (2)	50
(2.3.1.2) Synthesis of ternary [(La)Cu(8-HQ)(CH ₃ OH)](NO ₃), complex (7)	51
(2.4) Analytical Determinations and Characterizations	51
(2.4.1) Apparatus and Instruments	51
(2.4.2) Mass Spectroscopy	52
(2.4.3) Electron Paramagnetic Resonance Spectra	53
(2.4.4) Experimental Calculation of Excited State Dipole Moments	54
(2.4.5) Magnetic Susceptibility Measurements	57
(2.4.6) Thermal Analysis	57
(2.4.7) Quantitative Analyses of the Metal Cations	58
(2.4.7.1) Determination of Cu(II) ion	58
(2.5) Antimicrobial Activity	59
(2.5.1) Preparation of tested compound	59
(2.5.2) Testing for anti-bacterial and yeasts activity	59
(2.5.3) Testing for anti-fungal activity	60
(2.5.4) Standard references	60
(2.6) Theoretical Background of Molecular Modeling	60
(2.6.1) Quantum mechanics	61
(2.6.2) Molecular orbital (MO) theory	61
(2.6.3) Abinitio calculations	61
(2.6.4) Chemical accuracy	62
(2.6.5) Electronic energies and heats of formation	62
(2.6.6) Frontier orbitals and chemical reactivity	63
(2.6.7) The electron density	64
(2.6.8) Basic concepts	64
(2.6.9) Basis sets	64
(2.6.9.1) Split valence basis sets	65
(2.6.9.2) Polarized basis sets	66

(2.6.9.3) Diffuse basis sets	66
(2.6.9.4) Common basis sets	66

Chapter III

RESULTS AND DISCUSSION

Abstract	67
Introduction	68
Aim of this chapter	68
Results and discussion	70
(A) IR Spectra of the Prepared Ligands	71
(B) Mass Spectra of the Prepared Ligands	72
(C) ¹ H-NMR Spectra of the Prepared Compounds	74
(D) ¹³ C-NMR Spectra of the Prepared Compounds	75
(E) Electronic Spectra of ACC and its Hydrazones HL_a and HL_b	76
(F) Emission Spectra	77
(G) Solvent Effects on the Emission Spectra	83
i- Non-specific Interactions.	86
ii- Specific interactions	86
(H) Estimation of ground and excited state dipole moments	94
(I) Computational method	98
(J) Frontier Molecular Orbital Analysis (FMO)	98
(K) Global chemical reactivity descriptors (GCRD)	101
Conclusion	103

Chapter IV

Abstract	136
Aim of this chapter	137
Results and discussion	137
(A) IR Spectra	138
(B) Conductivity measurements	141

(C) Electronic spectra and magnetic measurements	141
(D) Electron paramagnetic resonance spectra (EPR)	142
(E) Thermal analysis	144
(F) Mass spectra	146
(G) Fluorescence spectra	153
Estimation of ground state and excited state dipole moments	158
(H) Antimicrobial studies	160
(I) Molecular modeling	163
Frontier Molecular Orbital Analysis (FMO)	163
(J) Conclusion	166

Chapter V

Abstract	201
Aim of this chapter	202
Results and discussion	203
(A) IR Spectra	203
(B) Conductivity measurements	208
(C) Electronic spectra and magnetic measurements	208
(D) Fluorescence spectra	210
(E) Mass spectra	214
(F) Thermal analysis	214
(G) Molecular orbital calculations	217
HOMO – LUMO Analysis	217
Molecular modeling and biological activity	219
(H) Antimicrobial Studies	221
(I) Conclusions	222
References	255
English Summary	268

List of Schemes

Scheme No.	Title	Page
Scheme 2.1	The synthetic pathway for the hydrazones (HL_a and HL_b) ligands.	49
Scheme 2.2	Tautomeric forms of the HL_a ligand.	49
Scheme 2.3	Tautomeric forms of the HL_b ligand.	50
Scheme 3.1	Structural formula of ACC , ACMHCA (HL_a) and ACMNPHTCA (HL_b) .	69
Scheme 3.2	Tautomeric structures of ACC .	70
Scheme 3.3	Tautomeric structures of HL_a .	70
Scheme 3.4	Tautomeric structures of HL_b .	70
Scheme 3.5	Mass fragmentation patterns of the HL_a ligand.	73
Scheme 3.6	Mass fragmentation patterns of the HL_b ligand.	74
Scheme 3.7	Resonance effect of electron-accepting of ACC , HL_a and HL_b .	92
Scheme 4.1	Mass fragmentation patterns of complex 2 .	134
Scheme 4.2	Mass fragmentation patterns of complex 5 .	135
Scheme 4.3	Mass fragmentation patterns of complex 6 .	136

Contents

Scheme No.	Title	Page
Scheme 4.4	Mass fragmentation patterns of complex 8 .	137
Scheme 4.5	Representative structures of the Cu(II) complexes 1-8 .	147
Scheme 5.1	The possible tautomeric structures of Cu(II) complex.	205
Scheme 5.2	Representative structures of the Cu(II) complexes 9-16 .	216

List of Tables

Table No.	Title	Page
Table 3.1	Physical and analytical data of the hydrazones, HL_a and HL_b organic compounds.	105
Table 3.2	Characteristic infrared frequencies (cm ⁻¹) of ACC and the hydrazones, HL_a and HL_b organic compounds.	106
Table 3.3	The ¹ H-NMR chemical shifts (ppm) of ACC and hydrazones HL_a and HL_b , ligands and their assignments.	107
Table 3.4	The ¹³ C-NMR chemical shifts (ppm) of the hydrazones, HL_a and HL_b , ligands and their assignments.	108
Table 3.5	Solvent parameters: ϵ (dielectric constant), n (refractive index), E_T^N (normalized Reichardt constant and their $f(\epsilon, n)$ functions	109
Table 3.6	Excitation, emission wavelength bands, extinction coefficient and quantum yield of 2-aminochromone-3-carboxyaldehyde (ACC) and its hydrazones HL_a and HL_b in different solvents at room temperature.	110
Table 3.7	Solvatochromic data of ACC and its hydrazones HL_a and HL_b ligands.	112
Table 3.8	Linear regression analysis of stokes shift <i>versus</i> solvent parameters of ACC and its hydrazones HL_a and HL_b compounds.	113
Table 3.9	The slope (m), Intercept (C), Correlation coefficient (r) and number of data points (n) corresponding to statistical treatment of spectral shifts.	116