



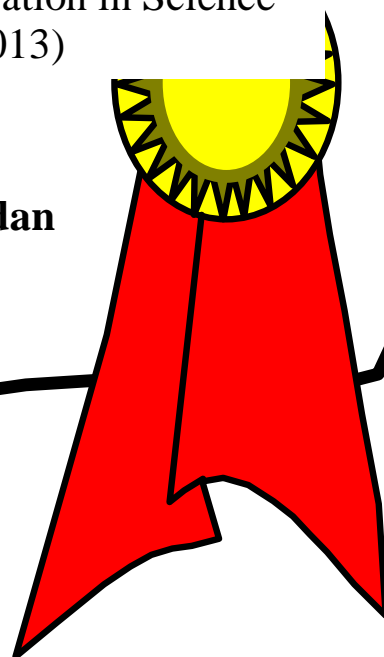
Department of Chemistry
Faculty of Education
Ain Shams University
Cairo - Egypt

Physico-chemical studies on some transition metal chelates

A Thesis Submitted by
Hany Magdy Ahmed

For
Master degree of the Teacher's Preparation in Science
(Inorganic Chemistry) (2013)

Under Supervision
Prof. Dr. Atef Ahamed Taha Ramadan
Prof. Dr. Ali Mahmoud Taha





Ain Shams University
Faculty of Education

Title Sheet

Title : physicochemical studies on some transition metal chelates

Candidate : Hany Magdy Ahmed

Degree : Master of the Teacher's Preparation in Science
 (Inorganic Chemistry).

Department : Chemistry

Faculty : Education

University : Ain Shams

Date of Award : / / 2013

Name : Hany Magdy Ahmed

Title : physicochemical studies on some transitions metal chelates&molecular orbital calculations.

Submitted to : Chemistry Department, Faculty of Education,
Ain Shams University

Abstract

$M(O-O)(N-N)_nX_n$, were prepared and characterized. The dissociation constants of HDMCHD as well as the formation constants of its complexes with some transition, lanthanide metal ions have been investigated potentiometrically in 50% (v/v) dioxane-water constant temperature. The thermodynamic parameters for HDMCHD chelate were evaluated and discussed. The data indicates monoprotic ligand and formation of complexes in molar ratio 1:1 and /or 1:2 (M:L). The solid metal complexes of the ligands with, Fe^{III} , Co^{II} , Ni^{II} , Cu^{II} , and Cd^{II} ions were isolated and characterized by elemental analysis, IR, electronic spectra as well as TGA, conductivity and magnetic susceptibility measurements. The data refer to the formation of mononuclear or binuclear complexes and various geometries according to type of the metal ions as well as the ligand used. The optimized structures for the free ligands and their complexes have been determined using Hyper Chem 7.5 program at (PM3) level. The theoretical data gave good correlations with the experimental data.

Acknowledgement

I wish to express my sincere gratitude to, Prof. Dr. Atef A. T. Ramadan; Professor of Inorganic and Analytical Chemistry, Prof. Dr. Ali M. Taha; Professor of Inorganic and Analytical Chemistry, Faculty of Education, Ain Shams University, for suggesting the line of the research and for following the progress of the work with keen interest, constant supervision, valuable discussion and criticism and for making this thesis possible in its present form.

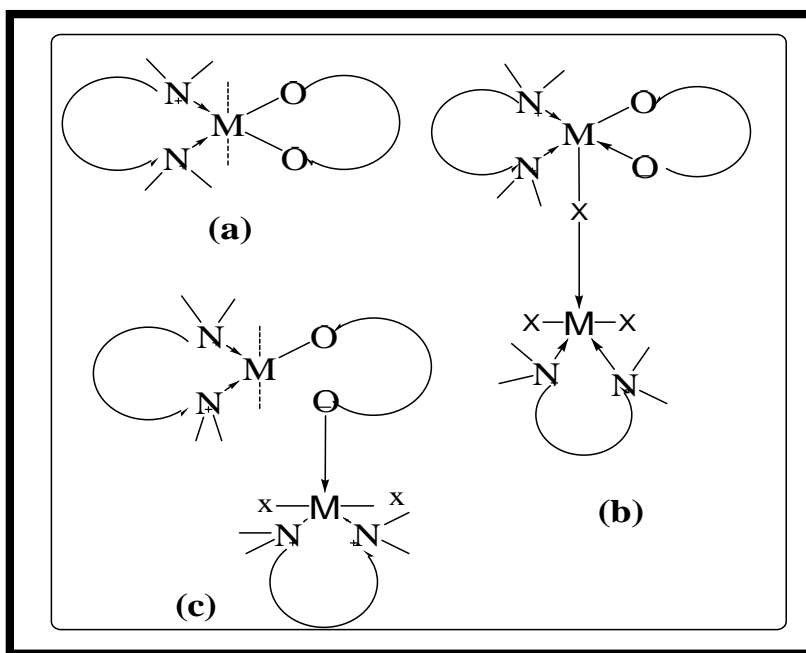
Many thanks to Prof. Dr. mostafa ismail; Head of Chemistry Department, Faculty of Education, Ain Shams University, Prof. Dr. Saeid M. Khalil; Former Head of Chemistry Department, Faculty of Education, Ain Shams University.

I would like to thank all staff member of Chemistry Department, Faculty of Education, Ain Shams University for their help and encouragement.

Aim of the Work

Complexes of the type $M(O-O)(N-N)$ have been reported as antimicrobial activities, antibacterial, and antifungal activities. However, the solvatochromic application of these complexes is very important. Owing to this paucity of information, we decided to investigate the reactivity and coordinating behavior and their solvatochromic application of these mixed ligand complexes.

The present study is planned to explore the dependence of coordination features and structure as well as solvatochromic behavior on the type of the metal cation and its counter anion as well as the experimental conditions of the current the copper(II) and Nickel(II)-complexes



Scheme I: The chelating modes of $M(O-O)(N-N)_nX_n$ complexes;

$M = Cu(II)$ or $Ni(II)$.

The present study comprises the following:

- Determination of the dissociation constant of 5,5-dimethyl cyclohexane-1,3-dione ligand (HDMCHD) as well as stability constants of its complexes with some divalent transition and trivalent lanthanide metal ions using pH-metric technique in 50% (v/v) aqueous-dioxane-and isopropanol solutions at 25 °C and ionic strength 0.1M.
- i- Isolation and characterization of the solid complexes of the (O-O) and (N-N) mixed ligands with Ni^{II} and Cu^{II} metal ions. The characterization based on the microanalytical, spectral, magnetic, molar conductance and thermal studies.

ii- Investigation of the solvatochromic properties of the isolated complexes in various organic solvents .
- Molecular orbital calculations of the present ligands and their copper(II) complexes using Hyper Chem 7.5 program at parametric method (*PM3*) level; and correlate the calculated structural parameters with the experimental data
- Antimicrobial screening of the present complexes toward some Gram-positive and Gram-negative bacteria; yeast and fungus.



Approval Sheet

Title : physicochemical studies on some transitions metal chelates

Candidate : Hany Magdy Ahmed teleb.

Degree : master degree. of the Teacher's Preparation in Science (Inorganic Chemistry)

Board of Advisors

Approved by

1- Prof. Dr. Atef Ahmed Taha Ramadan

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

2- Prof. Dr. Ali Mahmoud Taha

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

Date of presentation : / / 2013

Post Graduate Studies

Stamp of Approval / / 2013

Date of Approval : / 2013

Approval of Faculty Council / / 2013

Approval of University Council / / 2013

List of puplications

A. Taha, A.A.Taha and H.M.Ahmed 15-military college conference 2013.

Contents

List of abbreviations	i
List of Figures	ii
List of Tables	vi
List of Schemes	x
List of Structures	xii
Abstract	xiii

Chapter 1

Introduction

Introduction	1
1.I Literature Survey on solvatochromic complexes	1
1.II Literature Survey on metal carboxylate complexes	6
1.III Literature Survey on metal complexes of β -diketonates	26
1.IV Literature Survey on the Metal Complexes of miscellaneous	34

Chapter 2

Experimental & Theoretical Background

2.I Experimental	39
1- Materials	39
2- Purification of Solvents	40
3- Preparation of Solutions	41
4- Syntheses of $M_n(O-O)(N-N)_nX_n$ Complexes	42
5- Measurements	42
6- Quantitative Analyses of the Metal Cations	44
2.II Theoretical Background of pH-Metric Titrations	45
1- Acid Dissociation Constants	45
2- Chelate Stability Constants	46
2.III Theoretical Background of Molecular Modeling	49
1- Molecular Mechanics	49
2- Quantum Mechanics	51

Chapter 3

pH-Metric Studies

4.I	Dissociation Constants	60
4.II	Formation Constants	61
	Conclusion	65

Chapter 4

Structural Elucidation of Metal Complexes

4.1	Elimental analysis	75
4.2	IR Spectra	75
4.3	Electronic spectra ,Magnetic Studies and molar conductance measurements.	78
4.4	Electrochemical studies	83
4.5	Thermal Gravimetric Analyses (TG-DSC)	85

Chapter 5

Biological activity

5.1	Classifications of biological activity of metals	123
5.2.	Procedure of antimicrobial screening Parameters	124
5.3.	Antimicrobial studies of Ni(II) and Cu(II) complexes	125

Chapter 6

Molecular Modeling

6.I	Structural Parameters of the free ligands	129
6.II	Structural Parameters of metal complexes	130
Summary		156
References		161

List of abbreviations

H ₂ pheth	Phthalic acid
H ₂ Saly	Salicylic acid
H ₂ Suc	Succinic acid
H ₂ Ox	Oxalic acid
Hgly	Glycine
H aspi	Aspirin(acetylsalicylic acid)
HOHAP	O-hydroxy acetophenone
Hmesalt	Methylsalicylate
HDMCHD	5,5dimethylecyclohexane,1,3dion
HEAA	Ethyl acetoacetate
en	ethane-1,2-diamine
Me ₃ en	N,N,N'-trimethylethylenediamine
Me ₄ en	N,N,N',N'-tetramethylethylenediamine
Me ₅ dien	N,N,N',N',N''-pentamethyldiethylenetriamine
ΔH _f	Heat of formation
HOMO	High Occupied Molecular Orbital
LUMO	lowest Unoccupied Molecular Orbital
BZ	Benzene
dmp	2,9-dimethyl-1,10-phenanthroline
pydcH ₂	pyridine-2,6-dicarboxylic acid
tpmc	N,N, ⁰ N'',N'' ⁰ -tetrakis-(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetra decane
acac	acetylacetonate
TAE	tetraacetyethane
SMLR	stepwise multiple linear regression
H ₂ Mal	malonic acid
DEtEMal	diethylethoxyethylenemalonate
1,3-pn	1,3-propylenediamine
Et ₃ en	N,N,N'-triethylethylenediamine
Me ₄ pn	N,N,N',N'-tetra-methylpropylenediamine
medach	N-methyl-1,4-diazacycloheptane
bzac	benzoylacetonate
bipy	2,2'-bipyridine
phen	1,10-phenanthroline
H ₂ DACR	4,6-diacetyl-resorcinol
HOHBZ	o-hydroxy benzaldehyde

List of Schemes

No.	Subject	Page
i	The chelating ability of $M(O-O)(N-N)_nX_n$ complexes	xvi
3.1a	Tautomeric forms of HDMCHD.	60
6.2.1	electron redistribution in the square planar complexes.	132
6.2.2	electron redistribution in the octahedral planar complexes	132

List of Structures

No.	Subject	Page
6.2.1	The optimized of the proposed dehydrogenated structure of complex 1 $[\text{Cu}_2(\text{Pheth})(\text{Me}_4\text{en})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$	145
6.2.2	The optimized of the proposed structure of complex 3, $[\text{Cu}(\text{Saly})(\text{Me}_4\text{en})]$	145
6.2.3	The optimized of the proposed dehydrogenated structure of complex 6, $[\text{Cu}_2(\text{OX})(\text{Me}_4\text{en})_2](\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$	146
6.2.4	The optimized of the proposed structures of complex 8 , $[\text{Cu}(\text{GLY})(\text{Me}_4\text{en})]\text{NO}_3$	146
6.2.5	The optimized of the proposed dehydrogenated structure of complex 11 , $[\text{Cu}(\text{OHAP})(\text{Me}_4\text{en})](\text{ClO}_4)$	147
6.2.6	The optimized of the proposed dehydrogenated structure of complex 13, $[\text{Cu}(\text{ASP})(\text{Me}_4\text{en})]2\text{C}_2\text{H}_5\text{OH}$	147
6.2.7	The optimized of the proposed dehydrogenated structure of complex 17, $[\text{Cu}_2(\text{DMCHD})(\text{Me}_3\text{en})_2](\text{ClO}_4)_3 \cdot 2\text{C}_2\text{H}_5\text{OH}$	148
6.2.8	The optimized of the proposed dehydrogenated structure of complex 18, $[\text{Cu}_2(\text{DMCHD})(\text{Me}_4\text{en})_2](\text{ClO}_4)_3 \cdot 2\text{C}_2\text{H}_5\text{OH}$	148
6.2.9	The optimized of the proposed dehydrogenated structure of complex 20, $[\text{Cu}_2(\text{DMCHD})(\text{Me}_5\text{dien})_2](\text{ClO}_4)_2 \cdot 2\text{C}_2\text{H}_5\text{OH}$	149
6.2.10	The optimized of the proposed structure of complex 22 $[\text{Ni}(\text{Pheth})(\text{Me}_4\text{en})(\text{H}_2\text{O})_2]4\text{H}_2\text{O}$	149
6.2.11	The optimized of the proposed structure of complex 24 $[\text{Ni}(\text{Pheth})(\text{en})(\text{H}_2\text{O})_2]3\text{H}_2\text{O}$	150