



**METAL COMPLEXES FOR SOME BIS
PHENYL PYRAZOLYL METHANE**

**A Thesis
submitted by**

FOUZE MOHAMED EL-SAYED OMAR

B.Sc.

For

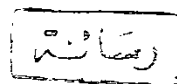
**THE MASTER DEGREE
in Science
(Chemistry)**

To

**CHEMISTRY DEPARTMENT
FACULTY OF SCIENCE
AIN SHAMS UNIVERSITY**

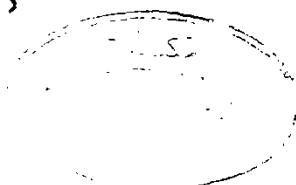
**work carried out in the
Faculty of Education
AIN SHAMS UNIVERSITY
CAIRO**

(1993)



2011/12/2
F M

015048



METAL COMPLEXES OF SOME BIS-PHENYL PYRAZOLYL METHANE LIGANDS.

Thesis Advisors

Approved

Prof. Dr. B. A. El-Shetary

Badrein El Shetary

Asst. Prof. Dr. Atef A.T. Ramadan

Atef A.T. Ramadan

Asst. Prof. Dr. Shaker J. Stefan

S. J. Stefan

Prof. Dr. A . F . M . Fahmy

A.F.M. Fahmy

Head of Chemistry Department



ACKNOWLEDGEMENT

The author wishes to express her deep appreciation to Dr. Bashier A. El-Shetary, Professor of Inorganic Chemistry, Faculty of Education, Ain Shams University, for his continuous supervision and the assistance he offered during the course of this work.

The authors wishes to express her gratitude to Dr. Atef A.T. Ramadan, Assistant Professor of Inorganic & Physical Chemistry and Dr. Shaker L. Stefan, Assistant Professor of Inorganic Chemistry, Faculty of Education, Ain-Shams University for their suggesting the point, valuable instructions and making this thesis possible to be in the present form.

The author appreciate the effort of Professor Dr. Ernő Brücher, Head of Inorganic and Analytical Chemistry Department and Dean of Lajos Kossuth University, Debrecen, Hungary in detection the thermal analysis for some of the solid complexes mentioned in this thesis.

Special thanks for Prof. Dr. S.M. Abd El-Moez, the Head of Chemistry Department, Faculty of Education, Ain-Shams University.

AIM OF THE WORK

The lanthanide and actinide elements constitute two families of metals which often exhibit similar chemical behaviour. This similarities is most easily observed with the cations in oxidation state (III).

The coordination chemistry of these elements has been studied nighter as intensively nor as extensively as that of the transition metal ions. One reason for this is that these elements have been less available generally than the transition metal elements. Although they are fairly abundant a lack of industrial application until a relatively few years ago caused many of the lanthanide elements to be fairly expensive. Increased intense in the use of these elements in phosphorous and lasers and as catalyst as well as improvement in the methods of separation has caused a substantial reduction of their cost. The lanthanide and actinide ions resemble the alkaline earth ions. They are type A or "hard acids" which have a strong preference for oxygen donor ligands. In the solid, it is possible to have coordination via nitrogen, sulphur, oxygen, etc..., but in aqueous solution, complexation almost always involves substitution of solvent water with their metal-oxygen bond by a ligand which forms another metal-oxygen bond.

A study of the thermodynamic parameters for the complexation reactions of Actinides yields valuable information concerning the nature of complex formed and

changes in the hydrogen of species in the reaction.

In the present study, a new concern arises towards the preparation of a new series of pyrazolone derivatives resulting from the condensation of 1-phenyl-3-methyl-5-pyrazolone with different substituted aldehydes to obtain bis condensation products.

Our aim is to study structure of these bis-condensation products and their pK^H values, also we studied the metal binding properties of the ligands with some actinide and lanthanide ions.

**The Following Paper has been accepted for Publication from
This Thesis:**

- "Complexation of The Uranyl (UO_2^{2+}) and Thorium (Th^{4+}) with Aryl bis(5-hydroxy-3-methyl-1-phenyl pyrazol-4-yl)methane", A.A.T. Ramadan, S.L. Setfan, B.A. El-Shetary and F.M. Omar, Department of Chemistry, Faculty of Education, Ain-Shams University, Roxy, Cairo, Egypt.

Dr W. Hemminger
Physikalisch-Technische
Bundesanstalt
Bundesallee 100
Postfach 3345
D-38023 Braunschweig
Germany

POSTCARD



1224-7

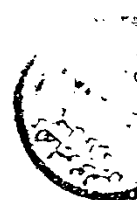


Dr. A.A. T. Ramadan
Dept of Chemistry
Faculty of Education
Ain Shams University
Cairo, Egypt
EGYPT

THERMOCHEMICA ACTA

Your paper entitled:

Complexation of the wavy



- ☒ has been received and will be considered for publication in Thermochimica Acta at the earliest opportunity.
- ☐ has been accepted for publication in Thermochimica Acta subject to editorial revision.
Proofs and a reprint form will be sent to you in due course.

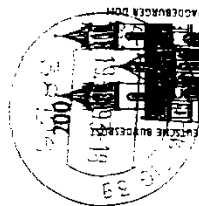
Editor

ELSEVIER SCIENCE PUBLISHERS
AMSTERDAM

16
61p

Dr W. Hemminger
Physikalisch-Technische
Bundesanstalt
Bundesallee 100
Postfach 3345
D-38023 Braunschweig
Germany

POSTCARD



Dr. Hef A. I. Ramadan
Department of Chemistry
Faculty of Education
Ain Shams University
CAIRO, EGYPT

THERMOCHEMICA ACTA

Your paper entitled:

Complexation of the uranyl



- ☐ has been received and will be considered for publication in Thermochemica Acta at the earliest opportunity.
- ☒ has been accepted for publication in Thermochemica Acta subject to editorial revision.
- Proofs and a reprint form will be sent to you in due course.

ELSEVIER SCIENCE PUBLISHERS
AMSTERDAM

Editor

He 1578

TO THE SOUL OF MY UNCLE
"FADEL EL-SAYED OMAR"

TO MY
HUSBAND,
"AHMED ABD-EL-SALAM"
FATHER & MOTHER,
ALL MY FAMILY

Table of Contents

Title	Page
<u>CHAPTER (I)</u>	
INTRODUCTION	1
(A) GENERAL BACKGROUND	1
(B) HYDRATED LANTHANIDES IN SOLUTION	3
(C) ORGANIC LIGANDS	6
(D) LITERATURE SURVEY ON 5-PYRAZOLONE DERIVATIVES ...	6
<u>CHAPTER (II)</u>	
EXPERIMENTAL AND THEORETICAL	14
(A) EXPERIMENTAL	14
(1) Materials	14
(2) Preparation of the Organic Ligands	14
(3) Preparation of Solid Complexes	16
(4) Purification of Solvents	16
(i) Methanol	16
(ii) Dimethylformamide	17
(5) Solutions	17
(i) EDTA Solution	17
(ii) Potassium Hydroxide	18
(iii) Preparation of Organic Ligand Solutions	18
(iv) Preparation of the Metal Ions Solutions	18
(6) Experimental Measurements	19

Title	Page
(i) Spectral Measurements	19
(ii) Conductance Measurements	19
(iii) Thermal Analysis	19
(iv) pH-Measurements	20
(B) THEORETICAL	22
(1) Acid Dissociation Constants	22
(2) Chelate Stability Constants	25
<u>CHAPTER (III)</u>	31
POTENTIOMETRIC STUDIES	31
(A) DISSOCIATION CONSTANTS	31
(B) INTERACTION OF THE LIGANDS (X-ArBPyM) WITH UO ₂ (II) AND Th(IV) INOS	33
<u>CHAPTER (IV)</u>	66
CHARACTERIZATION OF (X-ArBPyM) WITH UO ₂ (II) AND Th(IV) IONS BY ELEMENTAL ANALYSIS, IR SPECTRA AND THERMAL ANALYSIS	66
(A) RESULTS OF THE ELEMENTAL ANALYSIS	66
(1) UO ₂ ²⁺ Aryl bis(5-hydroxy-3-methyl-1-phenyl -4-pyrazolyl)-methane Complexes	67
(2) Th ⁴⁺ -Aryl bis(5-hydroxy-3-methyl-1-phenyl -4-pyrazolyl)-methane Complexes	

Title	Page
(Th-ArBPyM)	67
B) INFRARED SPECTRA	68
(1) Infrared spectra of Aryl bis(5-hydroxy -3-methyl-1-phenyl-4-pyrazolyl)methane Derivative (X-ArBPyM)	68
(i) Absorption at the 4000 - 2000 cm^{-1} region	68
(ii) Absorption at the 2500 - 1400 cm^{-1} region	69
(iii) Absorption at the 1400 - 1000 cm^{-1} region	69
(iv) Absorption at 1000 - 400 cm^{-1} region	70
(2) The Infrared Absorption Spectra of The Complexes	71
(i) The Infrared Absorption Spectra of Th^{4+} -(X-ArBPyM) Complexes	72
(ii) The Infrared Absorption Spectra of UO_2^{2+} -(X-ArBPyM) Complexes ...	74
(C) THERMAL ANALYSIS	75
TGA, DTG and DTA Thermograms of the Complexes	77
(i) (UO_2^{2+} -ArBPyM) Complex	77
(ii) (UO_2^{2+} -4- CH_3 -ArBPyM) Complex	78
(iii) (UO_2^{2+} -4- OCH_3 -ArBPyM) Complex ...	80
(iv) (UO_2^{2+} -4- NO_2 -ArBPyM) Complex	81

	Title	Page
(v)	(Th ⁴⁺ -ArBPyM) Complex	83
(vi)	(Th ⁴⁺ -4-CH ₃ -ArBPyM) Complex	84
(vii)	{Th ⁴⁺ -4-OCH ₃ -ArBPyM) Complex	86
<u>REFERENCES</u>		107
<u>Summary</u>		114
<u>Arabic Summary</u>		

CHAPTER (I) INTRODUCTION