STUDY OF THE REACTIONS OF SOME METAL CARBONYLS WITH SOME QUINOXALINE DERIVATIVES

A Thesis Submitted to

Chemistry Department, Faculty of Science, Ain Shams University
in the Fulfillment of the Requirements

For

The Degree of Doctor Philosophy in Science (Chemistry)

Presented By

Khalifa Abdoalsalam Alfallous
M.SC. in Chemistry (2004)

Under Supervisions of

Prof. Dr. Mohammed Fathi El-Shahat
Professor of Inorganic and Analytical Chemistry
Faculty of Science, Ain Shams University

Dr. Attia S. Attia
Assistant Professor of Inorganic Chemistry
Faculty of Science, Ain Shams University

Dr. Mostafa Yassen Nassar
Lecturer of Inorganic Chemistry
Faculty of Science, Banha University

2013

بسم الله الرحمن الرحيم

" وَيَسْأَلُونَكَ عَنِ الرُّوحِ قُلِ الرُّوحُ
مِنْ أَمْرِ رَبِّي وَمَا أُوتِيتُم مِّن الْعِلْمِ
إِلاَّ قَلِيلاً "

صدق الله العظيم

سورة الإسراء
آية (85)

Acknowledgement

First of all praise and thanks to **ALLAH** *providing me with time and effort to accomplish this thesis.*

It is a pleasure to express my deepest thanks and profound respect to my honored professor, Prof. Dr. Mohammed Fathi El-Shahat *Professor of Inorganic and Analytical Chemistry, Faculty of Science, Ain Shams University for his continuous encouragement and support that he gave me throughout the whole work. It has been an honor and a privilege to work under his generous supervision.*

I wish to express my deep gratitude to Dr. Attia S. Attia *Assistant Professor of Inorganic Chemistry, Faculty of Science, Ain Shams University for his enthusiasm, keen supervision, continuous encouragement and meticulous guidance and follow up throughout this work.*

A special tribute and cordial thanks are paired to Dr. Mostafa Yassen Nassar *Lecturer of Inorganic Chemistry, Faculty of Science, Banha University for his authentic guidance, meticulous supervision. He gave me a lot of her time, effort and experience to accomplish this work.*

At last but certainly not least, my special thanks to my family *specially* my wife *for support, help and understanding.*

Khalifa Abdoalsalam Alfallous

Published Work From The Thesis

Authors: Attia S. Attia , Ayman A. Abdel Aziz, Khalifa A. Alfallous, M.F. El-Shahat

Title: A novel bonding of 6,7-dichloroquinoxlaine-2,3-dione, DCQX, to two molybdenum (0) metal centers: Synthesis, characterization, biological activity studies and semiempirical calculations of $[(bpy)_2Mo(\mu_2\text{-}\kappa^2\text{:}\eta^6\text{-}DCQX)Mo(CO)_3]$ complex
Journal: Polyhedron 44 (2012) 238-244

Authors: Attia S. Attia , Ayman A. Abdel Aziz, Khalifa A. Alfallous, M.F. El-Shahat

Title: New diethoxo-bridged dinuclear Cr(III) complexes with derivatives

of the quinoxaline-2,3-dione ligand and 2,2`-bipyridine as a co-ligand: Syntheses, spectral characterizations, magnetic properties, antimicrobial inhibitory activities and interpretation of the electronic absorption spectra using the ZINDO/S-CI semi-empirical method

Journal: Polyhedron 51 (2013) 243-254

CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF SCHEME

LIST OF ABBREVIATION

Abbrev.	Full term
bpy	2,2` - bipyridine
^{1}HNMR	Proton Nuclear Magnetic Resonance
DCQX	6,7-dichloroquinoxaline-2,3-dione
DMF	Dimethyl formamide
DMQX	6,7-dimethylquinoxaline-2,3-dione
DMSO	Dimethyl sulphoxide
EtOH	Ethyl alcohol
IR	Infra-red
PM3	Semiempirical methods
QX	Quinoxaline
THF	Tertahydrofuran
UV-Vis	Ultraviolet-Visible
μ_{effct}	Effective Magnetic Moment

SUMMARY

SUMMARY

Complexes of chromium, molybdenum and ruthenium with derivatives of quinoxaline ligand, namely 6,7-dichloroquinoxaline-2,3-dione (DCQX) and 6,7-dimethylquinoxaline-2,3-dione (DMQX) have been synthesized and characterized.

Two novel complexes (bisdipyridine-quinoxaline derivatives-tricarbonyl dimolybdenum (0) of the general formula $Mo_2(bpy)_2(QX)(CO)_3$, (where QX = DCQX or DMQX) and bpy = 2,2′-bipyridine), was synthesized in two steps starting with the reaction of $Mo(CO)_6$ with bpy then followed by the addition of QX ligand. Initial characterization based on the elemental and mass analyses has suggested three possible structures. In the three suggested structures the QX ligand bonded to two Mo(0) metal centers; to one Mo metal through its C=O functional groups and the other through the aromatic ring forming η^6-arene type. In one of the suggested structures the QX ligand is bonded to $(bpy)_2Mo$ and $Mo(CO)_3$ moieties, whereas in the other structures the QX ligand is bonded to Mo(bpy)(CO) and *cis*-$(bpy)(CO)_2Mo$ or *trans*-$(bpy)(CO)_2Mo$ moieties. The IR studies were useful in assigning the coordination modes of the ligands especially in the carbonyl region of the spectrum. ^{1}HNMR studies in DMSO-d_6 displayed typical patterns corresponding to *cis*-$(bpy)_2M$ moiety. The electronic absorption spectrum of the complexes revealed two bands assignable to $Mo(d_\pi)\rightarrow arene(\pi^*)$ and $Mo(d_\pi)\rightarrow bpy(\pi^*)$

MLCT transitions. The thermogravimetric analysis gave more insight into the composition and the thermal stability of the complexes. The structural and vibrational behaviors of the $Mo_2(bpy)_2(DCQX)(CO)_3$ complex have been elucidated using semiempirical parameterized PM3 method. The biological activity studies revealed higher antimicrobial inhibition of $Mo_2(bpy)_2$-$(DCQX)(CO)_3$ complex compared with the free DCQX ligand. Whereas, the $Mo_2(bpy)_2(DMQX)(CO)_3$ complex showed only higher antifungal inhibitory activities compared with the free DMQX ligand.

With chromium hexacarbonyl $[Cr(CO)_6]$, two new diethoxo-bridged dinuclear Cr(III) complexes $[Cr(QX)(bpy)EtO]_2$ have been synthesized and characterized. The complexes were initially characterized on the basis of their elemental and mass analyses. The infrared studies were useful in assigning the coordination mode of the quinoxaline-2,3-dione ligand to the chromium metal. In addition, the presence of μ-ethoxo bridges was inferred from the characteristic vibrational bands in the IR spectra of both complexes. The structural and vibrational behaviors of both complexes have been elucidated using parameterized PM3 semiempirical method. The magnetic susceptibility measured at 298 K has indicated exchange interactions between the two Cr(III) centers. The observed effective magnetic moments have been correlated to the calculated Cr···Cr distances and Cr–O–Cr angles of the $Cr(OEt)_2Cr$ cores in both complexes. The ESR spectra have been recorded on powder samples at 298 K. The dominant quintet state