

**A THEORETICAL STUDY ON THE STRUCTURAL,
ELECTRONIC AND OPTICAL CHARACTERISTICS OF
TETRAAZA MACROCYCLIC COMPLEX**

NUR HALIMATUS SAADIAH BINTI ABDULLAH

UNIVERSITI SAINS ISLAM MALAYSIA

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TETRAAZA MACROCYCLIC**

Nur Halimatus Saadiah Binti Abdullah

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AUTHOR DECLARATION

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged

Date:

Signature:

Name: Name: Nur Halimatus Saadiah binti Abdullah

Matric No: 3191469

Address:

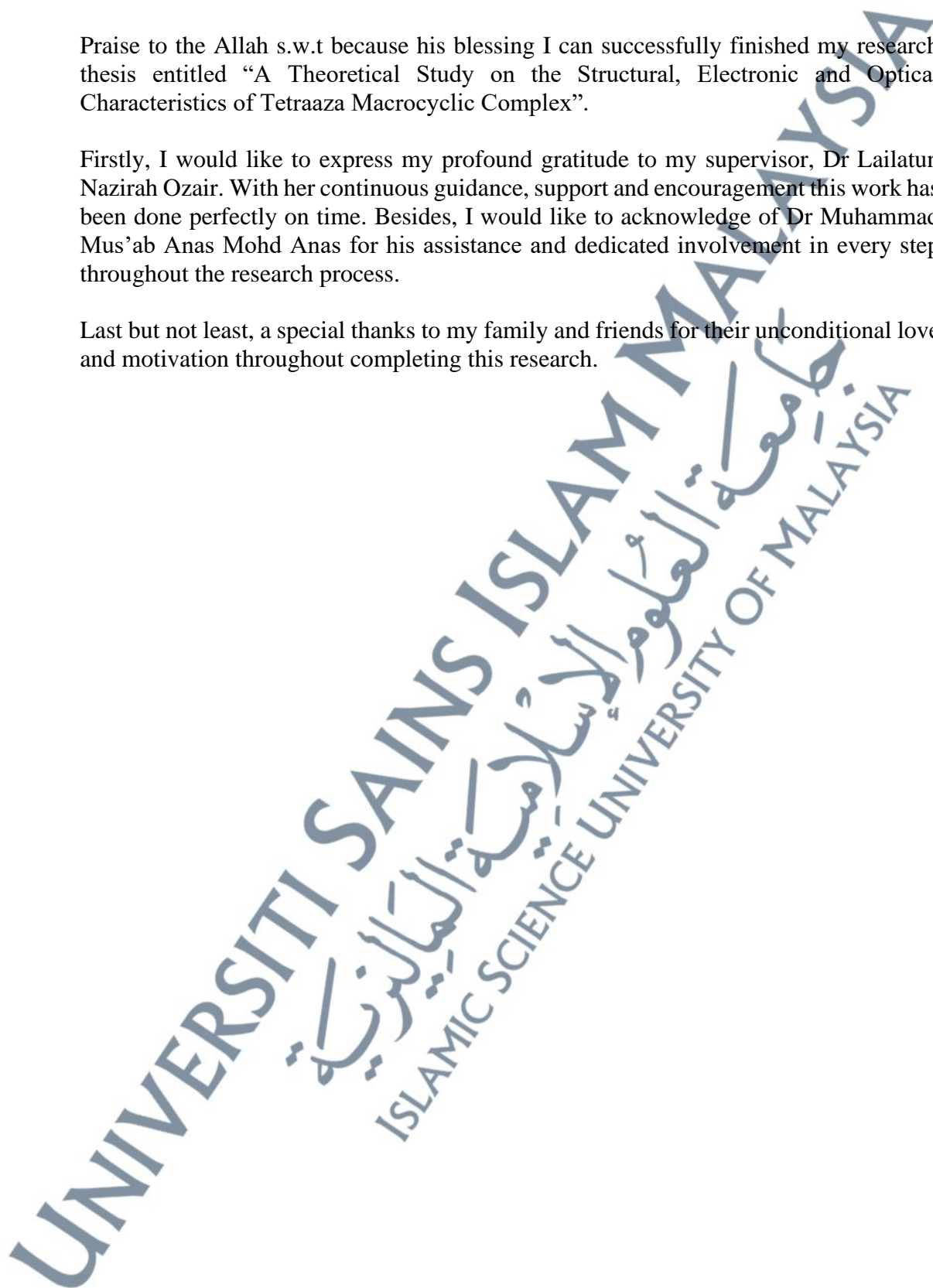
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ISLAMIC SCIENCE UNIVERSITY OF MALAYSIA

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ABSTRAK

Pd(II) kompleks yang mengandungi ligan tetraaza makrosilik telah menjadi topik penting dalam kajian penyelidikan terkini terutama dalam bidang pemangkinan, aplikasi rawatan sisa, dan bioperubatan. Ciri paling unik ligan tetraaza makrosilik ialah zarah nitrogen tinggi daya pilih terhadap ion logam peralihan dan tinggi kecenderungan membentuk sebatian makrosilik. Kaedah konvensional sintesis ligan tetraaza makrosilik ialah menjadikan ion logam peralihan sebagai agen templat mempunyai masalah semasa proses nyahkompleks kerana ion templat terlalu stabil. Kemudian, kaedah sintesis tanpa templat diperkenalkan yang menghasilkan ligan tetraaza makrosilik dan sebatian logam terproton. Bagaimanapun, hingga kini, sangat terhad kajian teori secara spesifik dilaporkan ke atas interaksi logam-ligan semasa pengkompleksan berlaku. Oleh itu, kajian ini telah memeriksa struktur Pd(II) ligan tetraaza makrosilik dan mengkaji sifat elektronik melalui pengiraan teori fungsi ketumpatan. Geometri molekul menunjukkan zarah Pd(II) berjaya menyuaikan diri dalam ligan makrosilik dan interaksi logam-ligan menyumbang pada kestabilan Pd(II) ligan tetraaza makrosilik. Kemudian, sifat optikal Pd(II) ligan tetraaza makrosilik telah disiasat pada keadaan teruja menggunakan teori sandaran masa fungsi ketumpatan dalam medium gas mendapati sempadan orbital molekul menunjukkan mobiliti elektron yang tinggi kerana sikit tenaga yang diperlukan semasa proses pemindahan elektron. Tindak balas optikal terhadap Pd(II) ligan tetraaza makrosilik dalam medium heksana, toluene, kloroform, metanol, asetonitril dan air menggunakan formalisme persamaan integral oleh model polarasi kontinum menunjukkan perubahan bererti pada nilai-nilai jurang tenaga, puncak penyerapan, dan hiperpolarisasi berbanding dalam medium gas.

ABSTRACT

Pd (II) complex containing tetraaza macrocyclic ligand has already been an important topic of current research studies, especially in catalysis, waste treatment application, and biomedical. The most unique properties of macrocycles containing nitrogen atoms are high selectivity towards transition metal ions and a high tendency to form macrocyclic compounds. The established method of synthesising tetraaza macrocyclic ligand by introducing a transition metal ion as a templating agent has demonstrated difficulties in the decomplexation process because template ions are too stable. Later, one pot synthesis of the non-template has been introduced resulting in protonated tetraaza macrocyclic ligand and metal complex. However, until today, there are limited theoretical studies that specifically reported on metal-ligand interaction in complexation. Therefore, this study examined the structure of the Pd(II) tetraaza macrocyclic ligand and further explored its electronic properties through density functional theory (DFT) calculation. The molecular geometry shows that the Pd(II) atom successfully fits in the macrocyclic ligand and metal-ligand interaction contributes to the stability of the Pd (II) tetraaza macrocyclic ligand. Then, the optical properties of Pd(II) tetraaza macrocyclic ligand were investigated at excited state using time-dependent density functional theory (TD-DFT) in gas medium observed frontier molecular orbitals indicate high electron mobility since only little energy is required for the electron transfer process. The optical responses on Pd (II) tetraaza macrocyclic ligand in hexane, toluene, chloroform, methanol, acetonitrile, and water environment using integral equation formalism of polarizable continuum model (IEF-PCM) show significant changes of the energy gap, absorption peaks, and hyperpolarizability values compared in gas medium.

الملخص

المركب Pd (II) الذي يحتوي على معقد ماكروسيكليلك تترازا قد أصبح موضوعاً هاماً في الدراسات البحثية الحالية، وخصوصاً في مجالات الكاتاليز وتطبيقات معالجة النفايات والطب الحيوي. من بين الخصائص الفريدة للماكروسيكليلك الذي يحتوي على ذرات النيتروجين هو انعتاقه العالي تجاه أيونات المعادن الانتقالية وميلاه الكبير لتكوين مركبات ماكروسيكلية. أثبتت الطريقة المثبتة لتخليق الماكروسيكليلك تترازا باستخدام أيون المعدن الانتقالي كعامل قوالب صعوبات في عملية الفك تترتب عليها ثبات كبير. في وقت لاحق، تم تقديم تخليق في مرحلة واحدة بدون قوالب، مما أدى إلى الحصول على الماكروسيكليلك المحمص المستخدم والمركب المعدني. ومع ذلك، حتى اليوم، هناك دراسات نظرية محدودة تقررت خصوصاً عن التفاعل بين المعدن والمركب في العملية التفاعلية. لذا، يهدف هذا البحث إلى دراسة هندسة مركب الماكروسيكليلك Pd(II) واستكشاف خصائصه الإلكترونية من خلال حساب نظرية الوظائف الكثافي DF. تظهر هندسة الجزيء أن ذرة Pd(II) تناسب الماكروسيكليلك وأن التفاعل بين المعدن والمركب يساهم في استقرار مركب الماكروسيكليلك Pd(II). بعد ذلك، تمت دراسة الخواص البصرية للماكروسيكليلك Pd(II) في الحالة المثارة باستخدام نظرية الوظائف الكثافية الزمنية المعتمدة (TD-DFT) في وسط الغاز، مما يشير إلى حركة إلكترونية عالية نظراً لاحتياج النقل الإلكتروني إلى كمية طاقة صغيرة جداً. تظهر الاستجابات البصرية للماكروسيكليلك Pd(II) في الهكسان، والتولين، والكلوروفورم، والميثانول، والأستونيتريل، والماء باستخدام نموذج معادلة التكامل للنظام المتغير القابل للتواصل (IEF-PCM) تغييرات كبيرة في الفجوة الطاقوية وذروات الامتصاص وقيم الانقطاع الهايبربولاريزابلية مقارنة بوسط الغاز.

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LIST OF ABBREVIATIONS

AM1	Austin model 1
B3LYP	Becke, three-parameters, Lee-Yang-Parr
CC	Coupled Cluster theory
CI	Configuration Interaction
DFT	Density functional theory
ECP	effective core potential
FMO	Frontier molecular orbital
GGA	Generalized Gradient approximation
HF	Hartree-Fock
HOMO	Highest occupied molecular orbital
IEF-PCM	integral equation formalism of polarizable continuum model
INDO	intermediate neglect of differential overlap methods
LANL2DZ	Los Alamos National Laboratory 2 Double-Zeta
LDA	Local Density approximation
LUMO	Lowest unoccupied molecular orbital
MM2	molecular mechanics 2
MM3	molecular mechanics 3
MMFF94	Merck molecular force field 94
NLO	Non-linear optical properties
Pd	Palladium
PM3	parametric method 3
STO-3G	Slater-type and Gaussian-type atomic orbitals
TD-DFT	Time dependent- density functional theory
UV-vis	Ultraviolet-visible