



Ministry of Higher Education
and Scientific Research
University of Babylon
College of Science
Department of Physics



Study of the Electrical Characteristics Behavior of Organometallic Structures

Submitted to the Council of the Department of Physics, College of
Science, University of Babylon

In Partial Fulfilment of the Requirements for Bachelor Degree of
Science in Physics

By

Ahmed Abbas Abd Kadhem

Supervised by

Assist. Prof. Dr. Mohsin K. Al-Khaykanee

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

(وَتِلْكَ الْأَمْثَالُ نَضْرِبُهَا لِلنَّاسِ وَمَا يَعْقِلُهَا إِلَّا الْعَالَمُونَ)

صدق الله العلي العظيم

(سورة العنكبوت: آية 43)

Acknowledgments

I extend my sincere thanks to my professor in the Department of Physics, grateful for his help, advice, and moral support throughout the university career that I spent, asking God Almighty to preserve and guide them and make them an asset for future generations of students. Assist. Prof. Dr. Mohsin K. Al-Khaykanee is the owner of high morals, kind words, wonderful advice, and abundance of knowledge. I thank him for helping me in completing our graduate research.

Supervisor Certification

I certify that the dissertation entitled " Study of the Electrical Characteristics Behavior of Organometallic Structures " was prepared under my supervision at the Department of physics / College of Science /University of Babylon, as partial fulfillment of the requirements for bachelor's degree.

Signature:

Assist. Prof. Dr. Mohsin K. Al-Khaykanee

Date: / / 2024

Abstract

Investigating the conductivities and thermoelectric properties for platinum metal complexes. The results were showed the type of ligands in the molecular complexes, which play a significant role in electrical and thermal properties calculations. The contact of the molecule with the electrodes along the plane of the molecule was given the molecule high ability to appear high conductance. Therefore, nitrogen atom in pyridyl rings those contacts with gold electrodes is more effective than the sulfur atoms. These molecules exhibit various conductance profiles, low conductance can be identified by molecule 1, and a higher conductance by molecule 4. We showed the molecule in the perpendicular to gold electrodes, and the presence of nitrogen atom in the position of contact with leads in place of sulfur gave the molecule high ability to an electron transfer.

Table of content

Chapter One : General Introduction	1
1.1 Introduction.....	1
1.2 Structure of Organometallic Compound	2
1.3 Classification of Organometallic Compounds	2
1.3.1 Ionic Bonded Organometallic Compounds:.....	2
1.3.2 Covalent Bonded Organometallic Compounds:.....	3
1.3.3 Multicenter Bonded Organometallic Compounds:	4
1.4 Properties of Organometallic Compounds.....	5
1.5 Importance and Uses of Organometallic Compounds	6
1.5.1 Importance	6
1.5.2 Uses.....	6
Chapter Two : Electrical Properties of Organometallic Compounds	2
2.1 Introduction.....	8
2.2 Platinum Metal Complexes.....	10
Chapter Three: Results and Discussion.....	11
3.1 Computational methods	12
3.2 Electrical Properties	14
3.3 Results.....	14
3.4 Conclusion	18
References	19



Chapter One

General Introduction

1.1 Introduction

The term “Organometallic compound” refers to a collection of substances that have at least one metal-to-carbon bond, where the carbon is a component of an organic group. Organometallic compounds make up a sizable class of substances that have been crucial to the advancement of chemistry as a discipline. In the lab and in industry, they are largely utilized as catalysts and as intermediates. Compounds like ferrocene, a surprisingly stable compound with an iron atom sandwiched between two hydrocarbon rings, are included in this family. There is a wide range in the physical and molecular characteristics of organometallic compounds. The majority are solids, especially those with ring-shaped or aromatic hydrocarbon groups, but some are liquids and some are vapors [1,2].

The specific type of carbon-metal bonds used affects the properties of the organometallic compounds in a significant way. Some of these bonds are regular covalent ones, in which atoms exchange pairs of electrons. Others are multicenter covalent bonds, in which there are more than two atoms involved in the connection. Ionic bonds are a third form, in which a single atom provides the bonding electron pair. Multiple links between carbon atoms hold the metal atom and the hydrocarbons together in donor-acceptor bonds. In covalent bonds between metal elements and carbon atoms, the electrons are typically distributed unevenly. The bond becomes polarized as a consequence, with one end being more negative than the other. The intensity with which the metal atom binds electrons determines the amount of polarization. Organometallic compounds vary in polar power from lead, which bonds with carbon with very Organometallic compounds are made up of a bond between a carbon atom and a metal atom. These compounds have a wide range of applications in various fields, including catalysis, materials science, and organic synthesis [1,2].

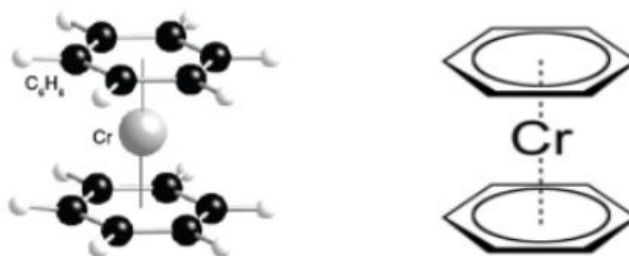


Figure (1.1): Organometallic compound

1.2 Structure of Organometallic Compound

The nature of the metal–carbon bond varies from ionic to covalent. The organometallic compounds have some effect on the nature of metal–carbon and these compounds have both organic and metal portions in which the metallic portion has greater importance. The electropositive nature of metal will be the ionic nature of the metal–carbon bond. In organometallic compounds, the carbon is bonded to an electropositive atom, which has a negative charge, whereas the metal has a slightly positive charge; hence, the organometallic compounds having the organic part behave as nucleophilic or basic [2].

1.3 Classification of Organometallic Compounds

On this basis of nature of metal-carbon bond organometallic compounds are classified into:

1.3.1 Ionic Bonded Organometallic Compounds:

The organometallic compounds of alkali, alkaline earth metals, Lanthanides and Actinides are predominantly form ionic compounds. These are generally colorless

compounds extremely reactive, non-volatile solids and insoluble in organic solvents.

Examples: $\text{Ph}_3\text{C}^- \text{Na}^+$, Cp_2Ca , $\text{Cs}^+ \text{Me}^-$, $\text{Na}^+ \text{Cp}^-$ [3].

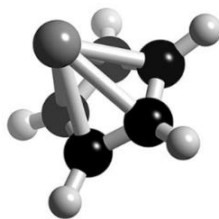


Figure (1.2): NaCp – Sodium cyclopentadienide

1.3.2 Covalent Bonded Organometallic Compounds:

a) σ - bonded organometallic compounds: These are the compounds in which carbon atom of the organic ligand is bonded to the metal by a 2 electron, 2 centered ($2e-2c$) covalent bonds. Generally formed by most of the elements with values of electronegativity are higher than 1. Examples: $\text{Ni}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$ [3].

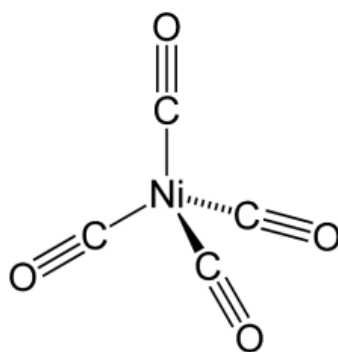


Figure (1.3): $\text{Ni}(\text{CO})_4$ -Nickel carbonyl

b) π - bonded organometallic compounds: These are alkene, alkyne or some other carbon group has a system of electron in π -orbitals overlap of these π - orbitals with vacant orbitals of the metal atom gives rise to arrangement in which the metal atom is bonded to several carbon atoms instead of to one. Examples:

$[(\eta^5 - \text{C}_5\text{H}_5)_2\text{Fe}]$, $\text{K}[\text{PtCl}_3(\eta^2 - \text{C}_2\text{H}_2)]$ (Zeise's salt)[3].

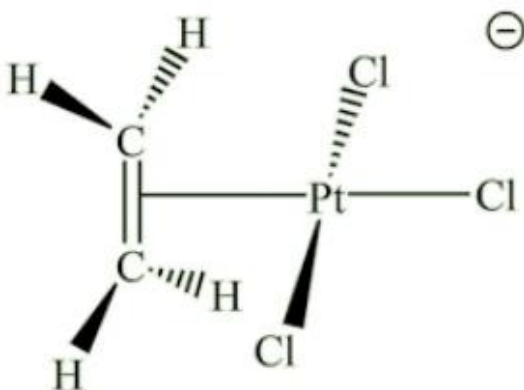


Figure (1.4): Zeise's salt- $\text{PtCl}_3(\eta^2\text{-C}_2\text{H}_2)$

1.3.3 Multicenter Bonded Organometallic Compounds:

The compounds in which a loosely bonded electron deficient species exist with the coordination of metal like Li, Be, Al... etc. Examples: MeLi or $(\text{CH}_3)_4\text{Li}_4$, Al_2Me_6 [3].

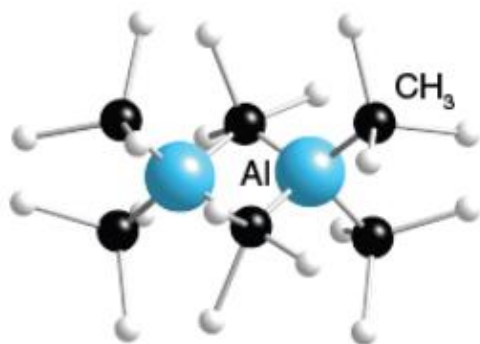


Figure (1.5): Al_2Me_6

1.4 Properties of Organometallic Compounds

Organic compounds are compounds based on carbon. They contain carbon and hydrogen, and can also contain other nonmetal elements such as oxygen, nitrogen, or halogen atoms. The properties of organic compounds are very different from the properties of inorganic compounds that you have been using up to this point. In this lab, you will explore some of the differences in the properties of organic vs. ionic substances. Most organic compounds are nonpolar and thus do not mix with polar molecules like water. Therefore, organic substances, in general, are insoluble in water. However, they are soluble in nonpolar solvents. Most ionic substances, on the other hand, are soluble in water and insoluble in nonpolar solvents. Organic compounds can be gases, liquids, or solids at room temperature. Ionic compounds are all solids at room temperature with very high melting points. Organic compounds have relatively low melting points and boiling points. The reason for these differences lies in the type of attractive forces holding the particles next to each other in each case. Ionic compounds consist of a vast array of alternating positive and negatively charged ions. Ionic substances are held together by very strong electrostatic forces and there are no individual molecules present. In order to melt an ionic compound, the ions must be able to move around each other, so a huge amount of energy is needed to break these strong electrostatic forces and thus ionic compounds have very high melting points. Organic compounds, on the other hand, consist of individual molecules held together by covalent bonds. The attractive forces between molecules consist of relatively weak London dispersion forces. Since the attractive forces between molecules are weak, it doesn't take much energy to disrupt them and thus organic molecules have low melting and boiling points [4].

1.5 Importance and Uses of Organometallic Compounds

1.5.1 Importance

Most organometallic compounds are used for synthesis purposes because bond polarity made them highly reactive [5, 6].

- 1) The Grignard reagent (R-Mg-X) organomagnesium halides are used in organic synthesis for organoboron and organolithium compounds.
- 2) Alkylaluminium compounds are used for organic synthetic purposes.
- 3) When an organometallic compound is used with titanium salts can act as a catalyst for the polymerization of ethylene and propylene that is unsaturated hydrocarbons.
- 4) The organometallic compounds of tin, mercury, and lead are used for commercial purposes. For example, organotin compounds are used as pesticides, pharmaceuticals, and stabilizers for polyvinylchloride (PVC) and also, they are used as fire retardants.
- 5) Metal carbonyls are used as catalysts in most reactions such as in the petrochemical industry.

1.5.2 Uses

Generally, organometallic compounds are used as reagents and catalysts, such as homogeneous and heterogeneous catalysts, for most synthetic reactions [7].

- 1) Organometallic compounds as homogeneous and heterogeneous catalysts: The organometallic compounds with a transition metal such as Rh i.e. $[\text{RhCl}(\text{PPh}_3)_3]$ act as catalysts for the hydrogenation of alkenes. Similarly, organometallic compounds such as trialkyl aluminum with titanium tetrachloride or trichloride are used as heterogeneous catalysts for the polymerization of alkanes.

2) Organometallic compounds for metal purification: During the process of metal purification initially, the impure metals are converted into carbonyls, further they should be decomposed to form pure metals.

3) Organometallic compounds for the synthesis of organic compounds: Organometallic compounds, such as organolithium and organomagnesium compounds, were used to prepare for organic synthesis.

4) Organometallic compounds can be used as reagents.

5) Organometallic compounds can be used as additives.

Agriculture and medicine: Organometallic compounds were also used in the field of agriculture and medicine. When seeds were treated with ethyl mercury chloride to prevent infection in plants. The organoarsenic compounds were used in the treatment of syphilis, in modern surgery, silicone rubbers were used.

Chapter Two
Electrical Properties of
Organometallic Compounds

2.1 Introduction

Metal complexes exhibit changed characteristic properties which depend on the nature of metal and the method arrangement of the ligand to which they are bound [8,9]. The arrangement of ligands is fixed to a given complex, but in some cases it is changing by a reaction that forms another stable isomer. Isomers contain the same number of ligands of complex, but have changed arrangements of their atoms attached to the central atom or ion of metal complex.

In the past decades, single-molecule is become more importance and interesting due to use it in an electronic element in circuitry and the control of energy gap comprising to semiconductor technology. Designing and construction of organometallic molecules is an active field of research due to their possible application to information technology, in particular the form of molecular-scale electronics devices, the biological environment, and complementing all views of transition metal-complexes applications in medicine [10].

For coordination compounds, the center metal atom in our molecules that we used to study electrical properties in this work, which bonded to an array of coordinating ligands.

The chemical formula of cis-platin is $\text{cis-[Pt(NH}_3\text{)}_2\text{Cl}_2\text{]}$, and is exemplified with a metal complex compound. The structure of cis-platin consists of a square-planar central platinum (II) binding to two chlorine ligands and two ammonia ligands. During the action, cis-platin molecule replaces the two chlorine ions with a pair of purine nitrogen atoms of DNA bases, inducing damages and triggering cell death. The substituent atoms in cis-platin are cis-conformer because these are set on the same plane in the molecule. The chemical structure of cis-platin can be written as

shown in **Fig. (2.1)**, in the common representations used for organic molecules [7, 8].

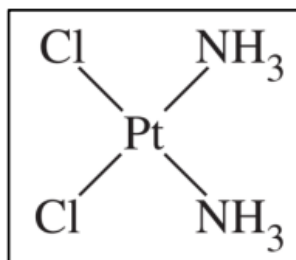


Figure (2.1): The chemical structure of cis-platin.

Moreover, the metal complexes that used it in platinum molecules with side groups that have also been known as potential components in molecular electronics applications in a future. Further, the investigation of charge transport across metal center and single-molecule ligand is interesting due to the respects a variation of the metal-organic bonding interactions. Hence, interfacial contact resistance is also expected to influence the charge-transfer properties of organometallic molecules. Initially, building intergraded circuits is ultimate goal of molecular electronics in the next generation of computer, which is super-fast as well as information storage. Now, many applications that are used of single molecules such as molecular witching, molecular transistors and sensors that have been recognized. There is widespread current interest in compounds that might behave as components in nanoscale electronic or photonic devices. In particular, pseudo-one-dimensional molecules that are capable of electronic transport between redox-active metal centers have been widely studied. Such “molecular wires” fall broadly into two categories: complexes where two or more metal centers are linked by a conjugated organic bridge, and those containing metal-metal bonds supported or unsupported by bridging ligands[5].

2.2 Platinum Metal Complexes

Some platinum metal complexes and compounds have high symmetric distribution of electron density and electrostatic potential and others make various behaviors for electron transfer. Platinum metal complex isomers have the same behavior of platinum centered compounds such as carboplatine and oxaliplatin used as drugs in clinical uses, where the ammine or bidentate ammine ligands and either chlorides or carboxylate are leaving groups [9].

The platinum metal complexes have high ability to interact with large molecules due to their symmetric in the space and to participate either in clinical use or under clinical trials as agents. All platinum metal complex compounds have electrophilic index greater than that for cis-platin and they are soft compounds.

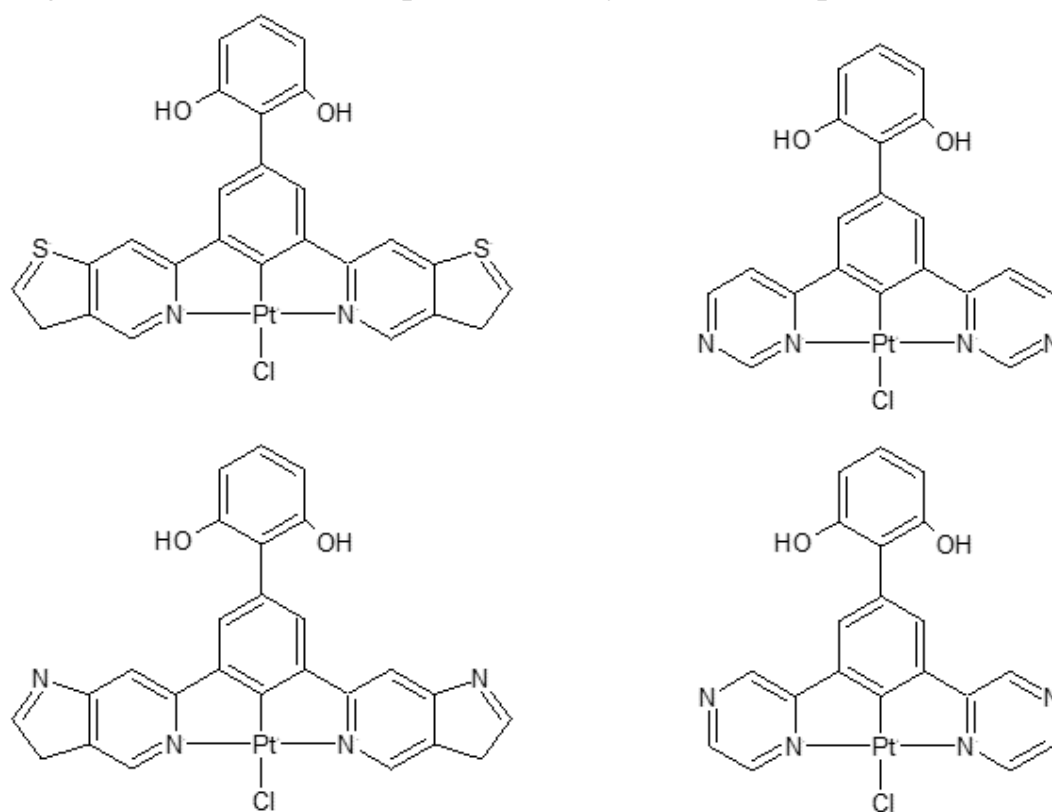


Figure (2.2): Platinum metal complexes

Chapter Three

Results and Discussion

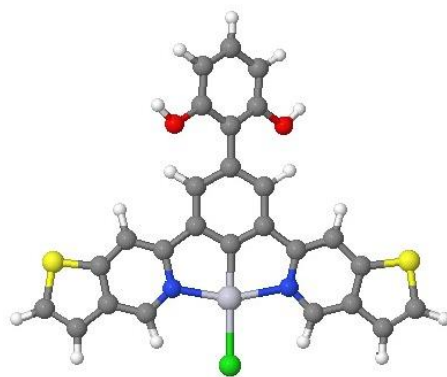
Chapter Three: Results and discussion

3.1 Computational methods

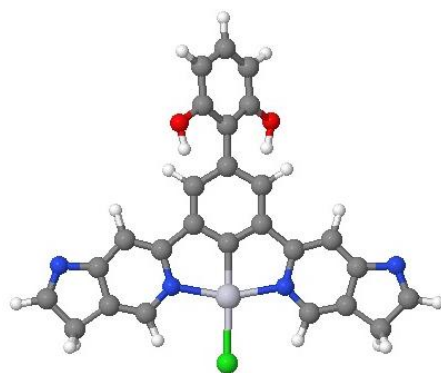
The full geometry optimization calculations have been performed for the studied platinum-metal molecular complexes using the three parameters Lee-Yang-Parr B3LYP density functional method DFT using Gaussian 09 package of programs. The computations were performed using the SDD basis sets for the atoms in these molecules. All calculations were carried out using the DFT SIESTA code [11-14].

The density mesh cut-off is set to be 250 Ry, and the molecular structures are allowed to fully relax until the force on each atom becomes less than 0.01 eV/Å. Then, using GOLLUM program [30] to compute T(E) [15].

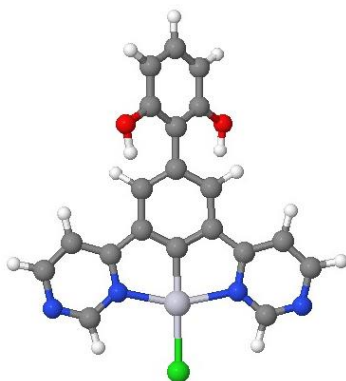
The **Fig. (3.1)** shows an example of these optimization calculations, which is Platinum's molecules. In our work, the main aim is to evaluate the metal-complexes selectivity in Platinum's molecules and understanding the nature of the metal complexes (Pt) chemical bond that contacts the complexes to backbone of the molecule[17].



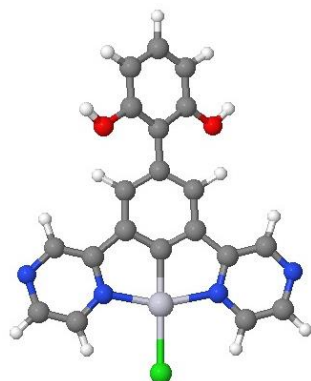
1



2



3



4

Figure (3.1): Molecular structures of Platinum's metal complex.

Chapter Three: Results and discussion

3.2 Electrical Properties

molecular structures of a series of Platinum's metal-complex molecules that have attention features in different applications such industry and Scientifics. The transition through metal-bridges complexes at molecular structures a significant role on the metal-bridges interactions. Hence, we have demonstrated to use Platinum's complex molecules to show the effect the metal-ligand atom on the electronics properties, and to know pi-conjugated system in all attempts before/or after replaced one carbon with nitrogen atoms in one or two the pyridine rings. We have used the Gaussian 09 package of programs in our calculations. The results show the bandgap decreased considerably with the type of metal-ligand atoms, which appear electronic applications at various LUMO-HOMO energy gaps.

3.3 Results

The molecules in **Fig. (3.2)** are four suggested platinum metal complexes, to study the electrical properties of Platinum's metal complex.

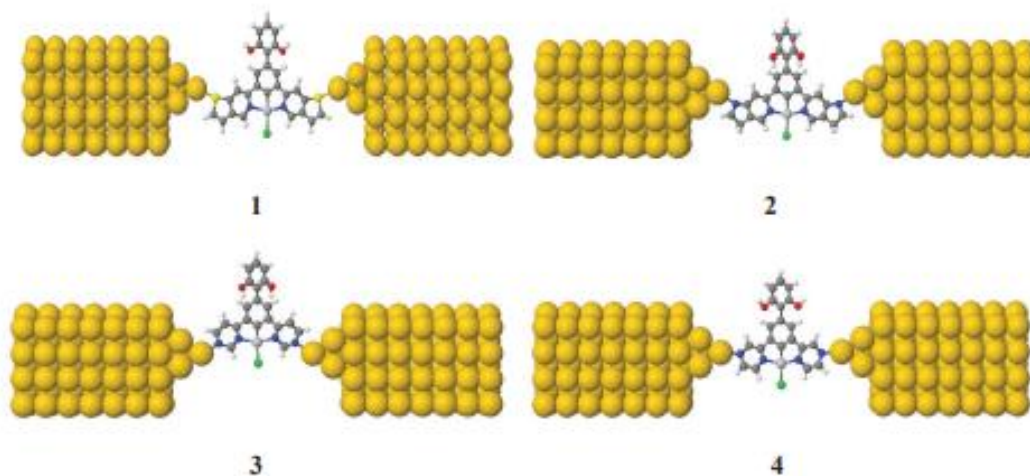
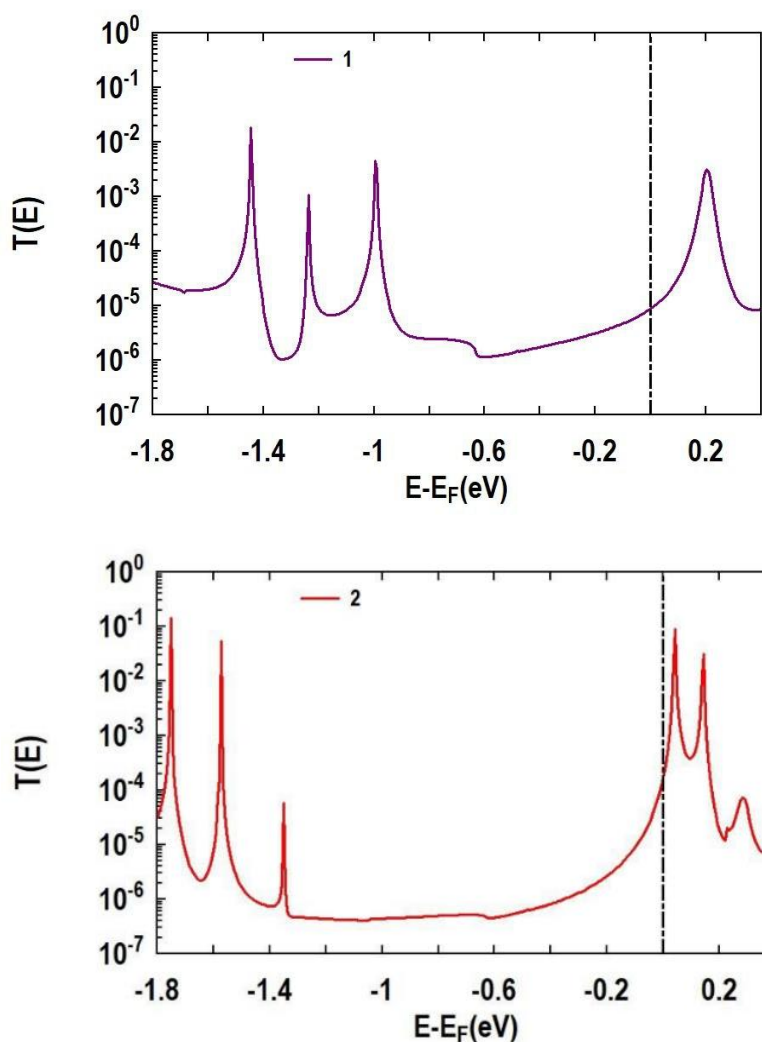


Figure (3.2): The relax structures of platinum metal complexes.

Chapter Three: Results and discussion

The molecules in **Fig. (3.2)** are four suggested platinum metal complexes were designed at Gauss View 5.0.8 program and initially relax at Gaussian09 package of programs, and then relax by using the SIESTA program. After the relaxation, each molecular structure was placed between two gold electrodes, and then each molecule structure plus limited layers of electrodes were for a second time allowed to produce the relax structures as shown in **Fig. (3.2)**



Chapter Three: Results and discussion

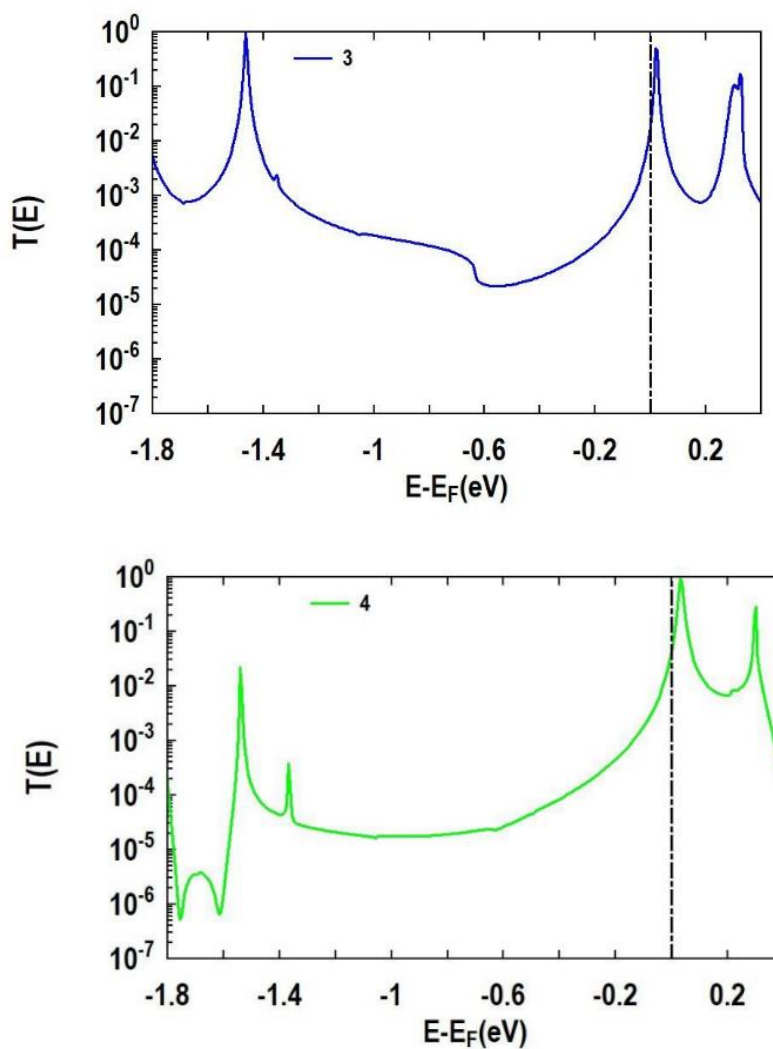


Figure (3.3): Zero bias transmission coefficient $T(E)$ as a function of electron energy

Fig. (3.3) illustrates the transmission coefficient $T(E)$ for the complexes under study, the values of $T(E)$ are as: 4(4.286×10^{-2}), 3(1.822×10^{-2}), 2(1.653×10^{-4}) and 1(8.741×10^{-6}). These results indicate the molecule in complex 4 in the same direction of electrodes and the presence of nitrogen atom in the position of contact with gold electrode in place of sulfur gave the molecule high ability to an electron transfer.

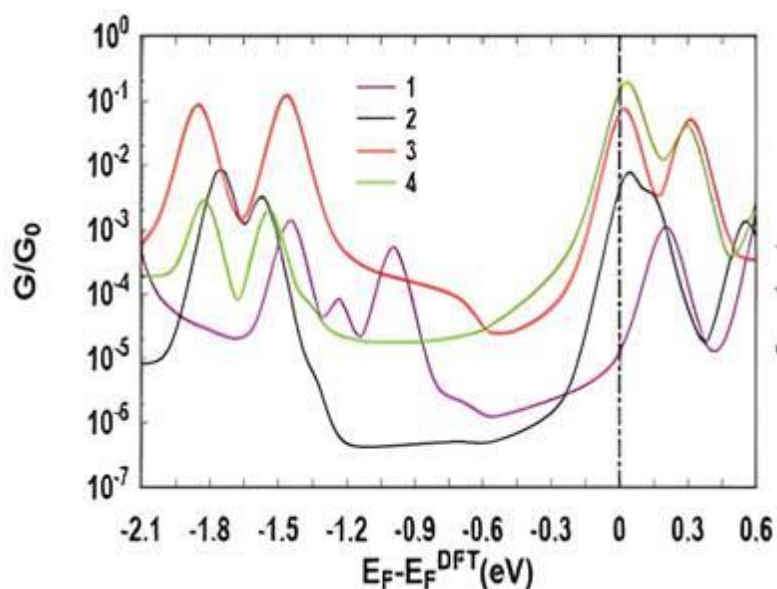


Figure (3.4): Electrical conductivity as a function of the Fermi energy.

Fig. (3.4) illustrates the electrical conductance G of the platinum metal complexes as a function of energy at room temperature, and it is as a function with various temperature. As seen in **Fig. (3.4)**, at Fermi energy $E_F=0$ the complexes 4 and 3 have the highest values of the electrical conductance, respectively. While, complex 1 has the lowest value of electrical conductance. Therefore, two notes can be observed from above results, the first that the connection of the molecule with the two electrodes gave complex 4 to has the highest $G(E)$ due to direct transmission of an electron, the second note that the presence of the phenyl at the connection part with the electrodes in place of naphthalene raises the conductivity of the complexes 3 and 4.

Chapter Three: Results and discussion

3.4 Conclusion

From above results, the initial relaxation for the complexes under study. The type of ligands in the complex plays a significant role in electrical properties calculations for the complexes. Nitrogen atoms in contact positions with gold electrodes are more effective than the sulfur atoms. The direction of the contact between the molecule and the electrodes determines the ability of the molecule to an electron transfer, the contact along the plane of the molecule gave the molecule high ability to appear high conductance. We showed the molecule in the same direction of electrodes and the presence of nitrogen atom in the position of contact with gold electrode in place of the anchor group gave these molecules high ability transferred electron.

References

- [1] “Organometallic Compounds - Definition, Details, Properties, and Applications.” Accessed: Jan. 25, 2024: <https://byjus.com/chemistry/organometallic-compounds/>
- [2] R. Chinen, “The Physical and Chemical Properties of Organometallic Compounds,” *Research & Reviews: Journal of Medicinal & Organic Chemistry RRJOMC/*, vol. 10, p. 3, 2023, doi: 10.4172/J.
- [3] P. Kumar, “VI Sem, B.Sc.,-Inorganic Chemistry Organometallic compounds ORGANOMETALLIC COMPOUNDS”.
- [4] G. B. Markandeya and S. Budagumpi, “Organometallic Compounds: The Fundamental Aspects,” 2023.
- [5] Mudi, S. Y., Usman, M. T., & Ibrahim, S. (2015). Clinical and industrial application of organometallic compounds and complexes: a review. *Am. J. Chem. Appl*, 2(6), 151-158.
- [6] A. F. Mushi, R. M. Obaid, and M. K. Al-Khaykane, “Controllable Structures of Metal-Ligand Bipyrimidine Molecules on Electronics Devices,” in *AIP Conference Proceedings*, American Institute of Physics Inc., Nov. 2022. doi: 10.1063/5.0121153.
- [7] Y. Tanaka, “Metal Complex Molecular Junctions as Thermoelectric Devices,” *Chemistry – A European Journal*, vol. 29, no. 29, p. e202300472, May 2023, doi: 10.1002/CHEM.202300472.
- [8] S. Medici, M. Peana, V. Marina Nurchi, J. I. Lachowicz, G. Crisponi and M. Antonietta Zoroddu, “Noble Metals in Medicine: Latest Advances”, *Coordination Chemistry Reviews* Vol. 284, pp. 329-350, (2015).
- [9] I. Turel, “Special Issue: Practical Applications of Metal Complexes”, *Journal of Molecules*, Vol. 20, pp. 7951-7956, (2015).
- [10] M. Gerloch and E.G. Constable, “Transition Metal Chemistry. The Valence Shell in d-Block Chemistry”, Published jointly by VCH Verlagsgesellschaft, Weinheim (Federal Republic of Germany) VCH Publishers, New York, NY (USA), (1994).

- [11] J. Ferrer, C. Lambert, V. García-Suarez, S. Bailey, S. Hatef, D. Manrique, Lancaster University, (2014).
- [12] E. Artacho, J. Gale, A. Garc, J. Junquera, P. Ordej, D. Sanchez-Portal and J. Soler, Fundacion General Universidad Autonoma de Madrid, (2013)
- [13] Fitts, D. D. (1999). Principles of quantum mechanics: as applied to chemistry and chemical physics. Cambridge University Press.
- [14] Soler, J. M., Artacho, E., Gale, J. D., García, A., Junquera, J., Ordejón, P., and Sánchez-Portal, D. (2002). The SIESTA method for ab initio order-N materials simulation. *Journal of Physics: Condensed Matter*, 14(11), 2745.
- [15] M. B. Baile, N. S. Kolhe, P. P. Deotarse, A. S. Jain and A. A. Kulkarni, “Metal Ion Complex -Potential Anticancer Drug- A Review”, *International Journal of Pharma Research & Review*, August, Vol. 4, pp. 59-66, (2015).
- [16] Ferrer, J., Lambert, C. J., García-Suárez, V. M., Manrique, D. Z., Visontai, D., Oroszlany, L., and Algharagholy, L. A. (2014). GOLLUM: a next-generation simulation tool for electron, thermal and spin transport. *New Journal of Physics*, 16(9), 093029.
- [17] Di Pietro, M. L., Stagno, C., Efferth, T., Omer, E. A., D’Angelo, V., Germanò, M. P., ... & Micale, N. (2022). Antileukemia Activity and Mechanism of Platinum (II)-Based Metal Complexes. *Molecules*, 27(24), 9000.

الخلاصة

دراسة التوصيلية والخواص الكهروحرارية لمعدّات فلز البلاتين. بينت النتائج نوع الليكاندات الموجودة في المعدّات الجزيئية والتي تلعب دوراً هاماً في حسابات الخواص الكهربائية والحرارية. إن اتصال الجزيء مع الأقطاب الكهربائية على طول مستوى الجزيء أعطى الجزيء قدرة عالية على الظهور بموصلية عالية. ولذلك فإن ذرة النيتروجين الموجودة في حلقات البيريدين التي تلامس أقطاب الذهب تكون أكثر فعالية من ذرات الكبريت. تُظهر هذه الجزيئات أشكالاً مختلفة للموصلية، ويمكن تحديد الموصلية المنخفضة بواسطة الجزيء 1، والموصلية الأعلى بواسطة الجزيء 4. لقد أظهرنا الجزيء بشكل متعامد مع أقطاب الذهب، ووجود ذرة النيتروجين في موضع التلامس مع الخيوط في مكان الكبريت أعطى للجزيء قدرة عالية على نقل الإلكترون.



جمهورية العراق
وزارة التعليم العالي والبحث العلمي
جامعة بابل كلية العلوم
قسم الفيزياء

دراسة سلوك الخصائص الكهربائية للهياكل المعدنية العضوية

بحث تخرج للطلاب

أحمد عباس عبد كاظم

مقدم الى مجلس كلية العلوم في جامعة بابل لنيل شهادة البكالوريوس في علوم الفيزياء

بإشراف

أ. م. د. محسن كاظم عبد حسين