Research Article

Quantum Mechanical Study Of the Interaction of Metal Ions with Porphyrin by DFT Method

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ABSTRACT

Metal porphyrins complexes consist of metal and porphyrin and they are formed by substitution of a metal cation with two protons porphyrin ring and creating a link between the four porphyrin ring and the metal. In the present research, the structure of the porphyrin,Metal ion bonded to porphyrin and Metal ion bonded dimers of porphyrin were calculated by middle tentative methods. The parameter Bond length, Energy and NBO analysis were calculated by density functional theory (DFT). It had high effect on bond strength and increased the heat of formation of them. Stability of all dimers were measured by calculation of Infrared spectrum. In bond length analysis of dimer, it was observed that the bond length of Metal ions decreases as charge factor increases. May increases the strength of Metal ions interaction to porphyrin. Also, results of studying the heterodimers were the same as previously observed and confirm the preceding consequences.

Keywords:*Metal Ions; Interaction; Porphyrin; DFT; IR Spectrum*
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1. Introduction

Porphyrin group of chemical compounds are defined on the basis of their chemical structure. Porphyrin part of body building proteins includes hemoglobin, myoglobin and some enzymes. Porphyrins and their derivatives in the process of energy conversion to electric light for photodynamic therapy Cancer have been applied laser technology. Porphyrins are the conjugate acids of ligands for bind metals to form complexes. The metal ion usually has a charge of +1 or +2. A schematic equation for these syntheses is shown:

H_2porphyrin + $[MLn]^{2+} \rightarrow$ M(porphyrinate)Ln−4 + 4 L + 2 H^+
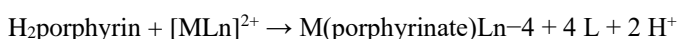
 Where M = metal ion and L = a ligand

are found extensively in nature. Hemoglobin and myoglobin are two O2-binding proteins that contain iron porphyrins. Various cytochromes are also hemoproteins. Several other heterocyclic are related to porphyrins. These include corrins, chlorines, bacteriachlorophylls, and corphins. Chlorines (2,3-dihydroporphyrin) are more reduced,

contain more hydrogen than porphyrins, and feature a pyrroline subunit. This structure occurs in a chlorophyll molecule. Replacing two of the four pyrrolic subunits with pyrrolinic subunits results in either a bacteriochlorin (as found in some photosynthetic bacteria) or an isobacteriochlorin, depending on the relative positions of the reduced rings. Some porphyrin derivatives follow Hückel's rule, but most do not.

The field of organic geochemistry,the study of the impacts and processes that organisms have had on the Earth, had its origins in the isolation of porphyrins from petroleum.

This finding helped to establish the biological origins of petroleum. Petroleum is sometimes "fingerprinted" by analysis of trace amounts of nickel and vanadyl porphyrins. Chlorophyll is a magnesium porphyrin, and heme is an iron porphyrin, but neither porphyrin is present in petroleum. On the other hand, nickel and vanadyl porphyrins could be related to catalytic molecules from bacteria that feed primordial hydrocarbons.

Porphyrins is their flexibility in terms of four criteria to be classified as is:

1. Saddle-shaped formation, 2. Fold formulated, 3. Dome formation, 4. Wavy formation

Metal porphyrins are complexes Metal of porphyrins, that formed the substitution of a metal cation with two protons of the porphyrin ring and obtained link between four porphyrin ring and metal. The size of the central cavity of the porphyrin almost 4/1Å, is a good state provides to bond with transition Main group metals. The metal ions play important roles in structure and function of proteins and other biomolecules. The rule of metals as cofactor is greatly magnified in activation of enzyme [1]. Magnesium is an essential element in biological systems. It occurs typically as the Mg2+ ion. It is an essential mineral nutrient for life and is presented in every cell type in every organism. For example, ATP (adenosine tri phosphate), the main source of energy in cells must be bound to a magnesium ion in order to be biologically active. Similarly, magnesium plays a role in the stability of all polyphosphate compounds in the cells, including those associated with DNA and RNA synthesis [2]. Trace amounts of lithium are present in all the organisms. The element serves no apparent vital biological function, since animals and plants survive in good health without it. Non-vital functions have not been ruled out. The lithium ion Li+ administered as any of several lithium salts has proved to be useful as a mood-stabilizing drug in treatment of bipolar disorder, due to neurological effects of the ion in the human body. Long-term calcium deficiency can lead to rickets and poor blood clotting and in case of a menopausal woman [3], it can lead to osteoporosis, in which the bone deteriorates and there is an increased risk of fractures. This project will examine the interaction of metal ions with porphyrins as the first step to investigate the interaction of these porphyrins with various metal ions and the effect of metal ions on the structure and enthalpy and once porphyrins and porphyrin with metal ions is calculated bond length. So, the purpose of this research is to investigate the stability of the metal ion in the porphyrin structure and the final structure breaks or as porphyrin is stable complexes with metal ions and also stable. As a result, the final structure is stable development of our approach to the impact of metal ions on the structure of the human body Systems biology is the study of the ecological and biological systems are used [4-12].

2. Computational Methods

Because all the calculations are theoretically physical chemistry is the best way to get to the key points and detailed empirical search of porphyrins in the laboratory of molecular ion with gaussian03 method. The structure of each species in this research include; porphyrin, metal ions attached to porphyrin and Metal ions bonded dimer of them were optimized fully by restricted B3LYP with 3-21G , 6-31G and 6-311++G** levels and gaussian03 package. Energy parameters, IR spectrum of each species were calculated through using method and basis set described beforehand. In the search of quantum mechanical study of the interaction of metal ions with porphyrin by DFT method in the field of software where not detail checked.

3. Result and Discussion

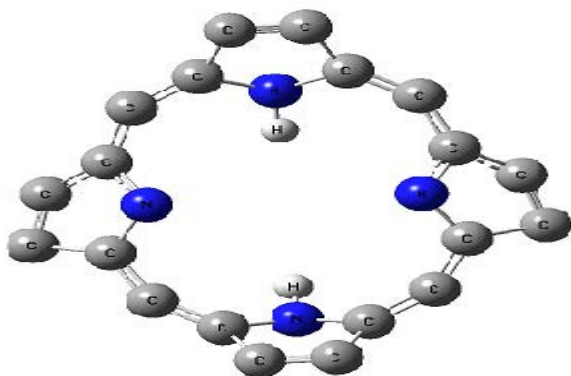Porphyrin is building block of Metalo-porphyrin which is shown in Fig.1.

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Fig.1. optimized structure for porphyrin

Table 1. Result comparison value , enthalpy , Charge and to Bond length structure dimer by DFT method

ROW	Type molecule	The enthalpy of formation (KCal/Mol)	Charge metal ions	Bond length M-N
1	Porphyrin	-975.029	-	2.37679
2	complex of Magnesium-porphyrin	-1173.031	1.84485	2.28658
3	complex of lithium - porphyrin	-987.4074	0.46	2.27434
4	complex of calcium-porphyrin	-1657.150	1.96110	2.26965
5	magnesium ion dimer of Porphyrin	-1612.83	1.77308	2.17280

General formula Interaction porphyrin with metal ions is shown at Eq1:

Porphyrin + Metal ions bonded to porphyrin   ⟶   Metal ions bonded dimers of porphyrin
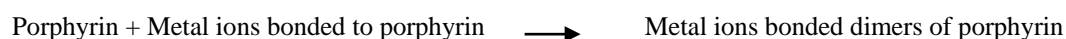
Structure and stability of Porphyrin, complexity of Metal ions with Porphyrin and Metal ions bonded dimer of them Structure of species involve in formation of dimers of porphyrin include; Metal ions bonded to porphyrin and Metal ions bonded dimer of them was calculated by methods as mentioned previously. The optimized structure of the Metal ions bonded to porphyrin and magnesium ion bonded dimer of them respectively are shown in Fig.3. Fig.4. and Fig.5.
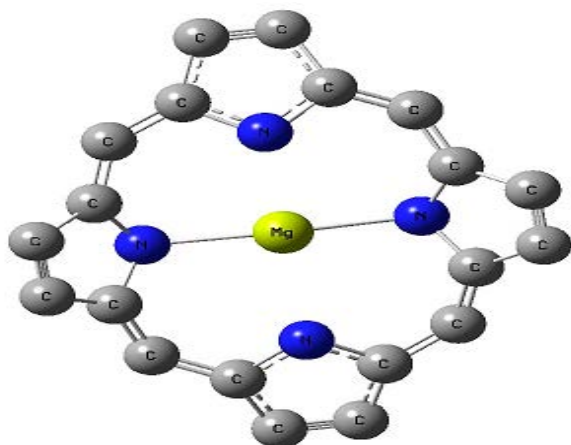
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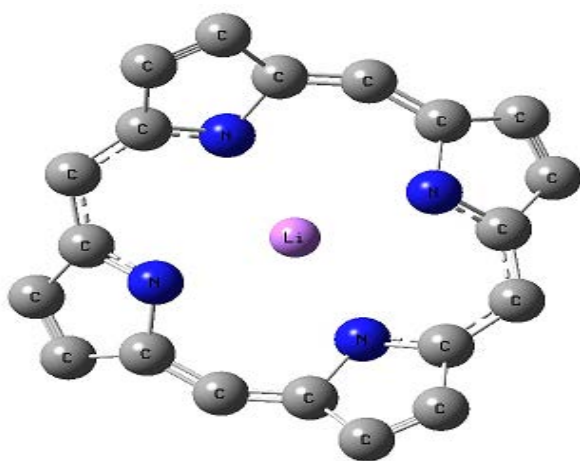**Fig.2.** Optimized structures complexes of magnesium ion and porphyrin.

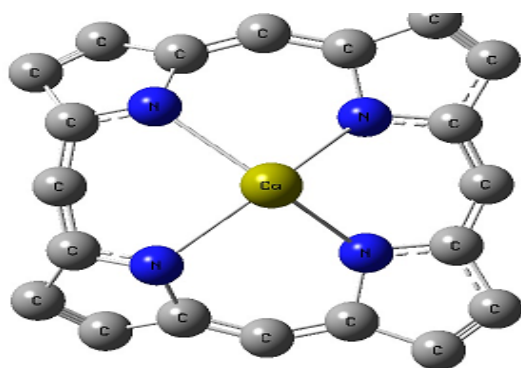**Fig.3.** Optimized structures complexes of lithium ion and porphyrin.

Fig.4. Optimized structures complexes of calcium ion and porphyrin.
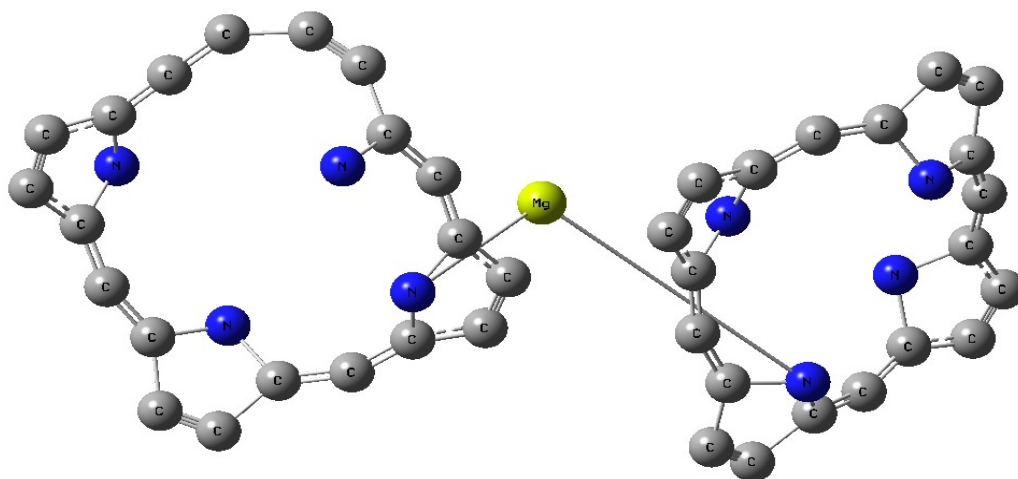
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Fig.5. Optimized structures magnesium ion bonded dimer of porphyrin

After obtaining the optimum structure for each molecule, the natural orbital analysis of them was done and then the partial charge for them extracted. Finally, the thermodynamic properties of each species were calculated. Structure of each porphyrin, Metal ion complex and Metal ion bonded dimer of them were optimized by method and basis sets mentioned previously in two conformations. The stability of the Metal ions bond complex was estimated by considering the IR spectrum of them. In Fig.6, Fig.7 and Fig.8, The structure of Metal ion bonded of porphyrin in IR spectrum of them are shown.
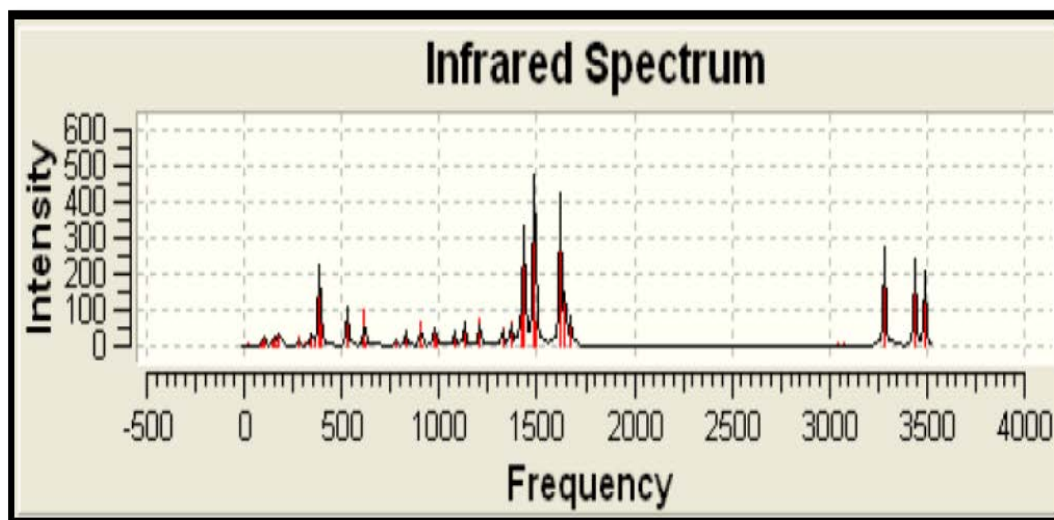

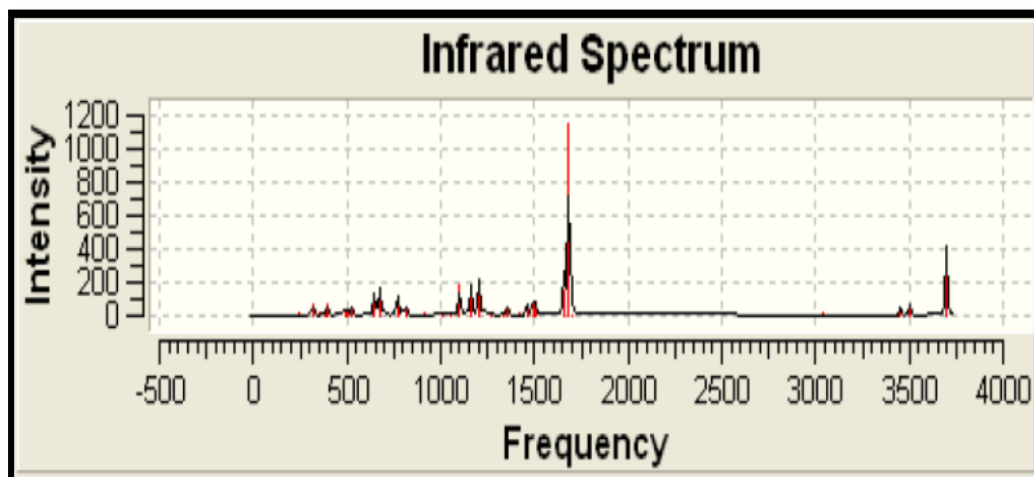**Fig.6.** IR Spectrum the structure of Magnesium ion bonded dimer of porphyrin

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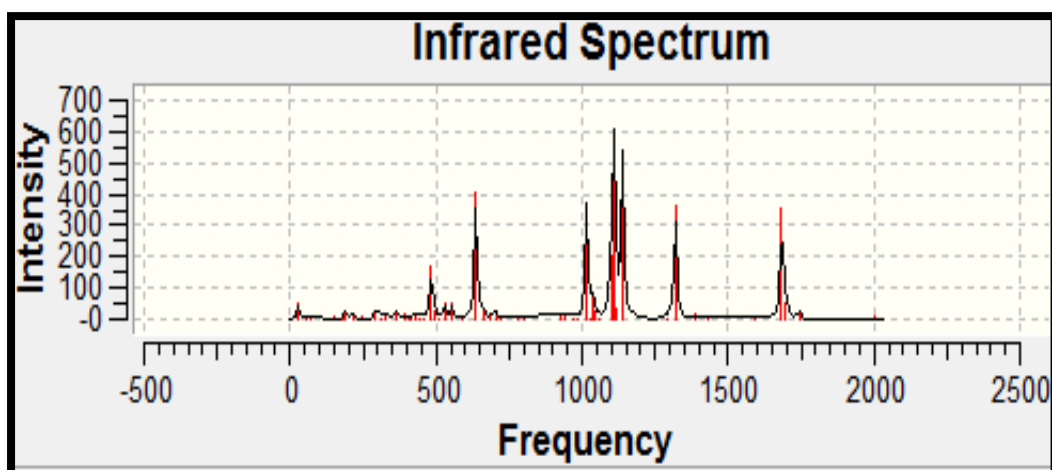**Fig.7.** IR Spectrum the structure of lithium ion bonded dimer of porphyrin

Fig.8. IR Spectrum the structure of calcium ion bonded dimer of porphyrin

Since observing the IR spectrum of the complex shows no negative vibrational mode in its spectrum, the dimers are considered stable. Bond lengths and enthalpy of formation of each Metal ions bonded complex: In this section the M-N bond lengths which show the strength of the M-N bond were calculated for each substituted Metal ions bonded complex. The result of M-N bond length versus Charge factor is shown in Fig.9
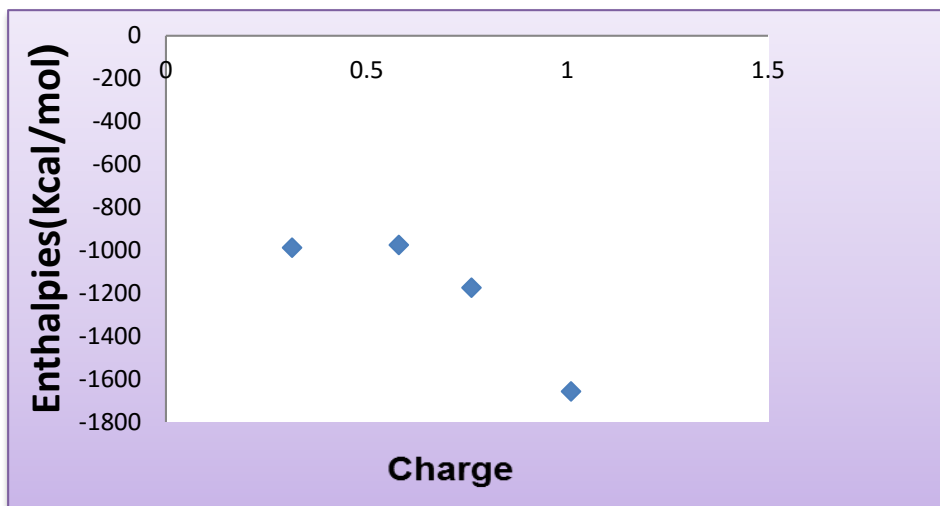
Fig.9. The enthalpy of formation for the dimer versus Charge factor

The enthalpy of formation was calculated by Eq.2:

$$\Delta H = \sum_{products} H_{prod} - \sum_{reactants} H_{react}. \quad Eq2$$

The enthalpy of formation of Metal ions bonded complex of porphyrin versus Charge factor is shown in Fig.10
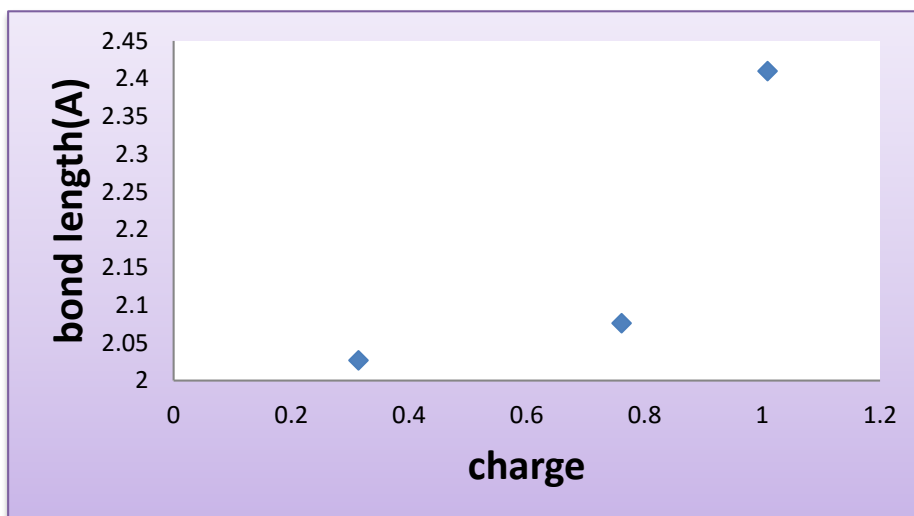

Fig.10. bond length the metal ions dimer of porphyrin versus charge

5. Conclusions

Structure and stability of Metal ions bonded Dimer of porphyrin as interaction of Metal ions with Inorganic compounds, were calculated by DFT calculations. Stability, bond length and energy analysis were performed to study the nature of Metal ions interaction porphyrin and to understand the effect of metal on strength of interactions. After optimization of the structure of homodimer, charge, bond length and energy analysis were done. Stability of all dimers were measured by calculation of Infrared spectrum. In bond length analysis of dimer, it was seen that the bond length of Metal ions decreases as Charge factor increases. This indicates that the structures are created in the

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best form stable complexes with porphyrins and the resulting structure can be used as ice in the biological and medical systems into target cells without damage to the issues and to feed supply cells.

REFERENCES

[1] *J.A. Cowan*, BioMetals.15, 225–235, 2002.

[2] Bertini*, I, Gray H.B, Lippard, S. J, Valentine, J.S*, Bioinorganic chemistry, University Science Books, Mill Valley, California ,1- 611,1994.

[3] *K. Sven, G. Helmar,* J. American Che Society.132 (35), 12492-12501, 2010.

[4] *Gerlt. J, Babbitt. P. C*, Arch, 433, 59–70, 2005.

[5] *D. Grueninger, G.E. Schultz,* New York.359, 787–797, 2006.

[6] *J.R. Knowles,* Annu Oxford.49, 877–919, 1980.

[7] *T. M. Larsen, J.E. Wedeking*, Biochemistry Oxford. 30, 4 349 – 4358, 1996.

[8] *M.E. Maguire, J.A. Cowan,* BioMetals.15, 203–210, 2002.

[9] *M. Nowotny, W. Yang,* Emboj. 25, 1924–193- 2006.

[10] *Y. Peeraer, A. Rabijns, J. Collet, E. VanScaftingen, C. De. Rante*, Eur. J. Biochem, 2713421–3427, 2004.

[11] A. *Pingoud, M. Fuxreiter, V. Pingoud, W. Wende,* Life Sci, 62, 685–707, 2005.

[12] *T.A. vSteitz, J.A. Steitz,* Natl. Acad. Sci. U.S.A, 90, 6498–6502, 1993.