Structural and Electronic Properties of Cis-platin Metal Complex: B3LYP-SDD/DFT Calculations

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Abstract—*Current work deals with the structural and electronic properties of the cis-platin by employing the B3LYP density functional theory with SDD basis sets at the Gaussian 09 package of programs. We showed a good relax was obtained for the cis-platin. The great contribution for constructing the molecular orbitals is due to the outer electrons in the platinum metal with few contributions from the p-orbitals of the ligands, cis-platin has insulating behavior. Also, the cis-platin has low electronic softness and it needs high excitation energy to electron transfer or to accepting an electron from the surrounding species.*

Keywords: *cis-platin, SDD basis sets, ionization energy, softness and electrophilic index.*

I. INTRODUCTION

Since the discovery of the activity of one of the mosteffective anticancer compound [cis-(NH3)2PtCl2],cis-iaminedichloroplatinum(II),where clinically named cis-platin thousands of platinum complexes have been synthesized and evaluated for their anticancer activity. Cis-platin was first discovered and synthesized by Peyrone in 1844but, unfortunately, its biological activity was discovered much late by Rosenberg and et al.,its represented the first inorganic metal complex compound introduced in clinical using for the treatment of the cancer[1-5]. Cis-platin remains in the middle of the most widely used platin chemotherapeutics, with particular effectiveness in the treatment of cancer.The pharmacodynamics properties of Cis-platin can also be modified in a markedly diverse way by targeting biological substrates distinct from DNA.. Cisplatin is a prototype of several thousand platinum[6-12]. Quantum chemical studies of the molecular and electronic structure, and prediction of spectroscopic characteristics of pharmacologically active compounds,

have always been challenging for computational chemists. Moreover, such data are quite useful for better understanding the reactivity of the drugs with physiological target molecules[2,5].

II. COMPUTATIONAL DETAILS

The calculations in present work are carried out theoretically by employing three parameters B3LYP(Becke's three parameter exchange with Lee, Yang, and Parr correlation functional) density functional theory and SDD (Stuttgart Dresden triple zeta ECPs (Effective-Core Potential))basis sets. The SDD basis sets possible quality for the system of interest for heavy metals use relativistic ECPs,it ispowerfully recommended for the heavy metals [14,15].

III. RESULTS AND DISCUSSION RESULTS

Fig. 1 represents the relax structure of cis-platin compound. The standard orientations as Cartesian coordinates in Angstroms for all atoms in the studied compound were listed in Table 1. Table 2 illustrated the resultant theoretical optimized parameters for the studied structure involve the bond length in Angstrom A° and bond angle in degree. As shown, the calculated values of bonds and the angles using SDD basis sets in present study are in good agreement with the experimental data[16].
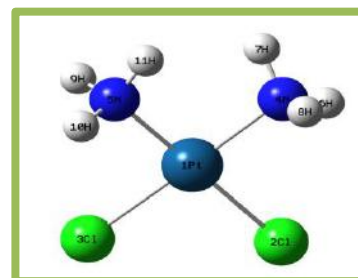

Fig.1: The relax structure of cis-platin.

Table.1: The standard orientations for all atoms in the cis-platin.

Atom	X	Y	Z
Pt	-0.000007	0.195450	-0.000010
Cl	1.781581	-1.402826	0.000049

Cl	-1.781643	-1.402763	-0.000028
N	1.599444	1.570299	-0.000040
N	-1.599310	1.570413	0.000083
H	2.407470	0.928257	0.000079
H	1.618117	2.151830	-0.841352
H	1.618001	2.152118	0.841063
H	-1.617473	2.152503	-0.840847
H	-2.407492	0.928601	-0.000437
H	-1.617949	2.151639	0.841599

Table.2: The optimize parameters of the cis-platin.

Geometric parameter	Present work	Experimental[16]	Theoretical [6]	
			method A	method B
R(N-H)	1.022-1.032) A°(	1.00	1.04	1.04
R(Pt-N)	2.049 A°	2.054	2.088	2.094
R(Pt-Cl)	2.393 A°	2.318	2.374	2.323
A(N-Pt-N)	89.671 deg.	90.2	100.2	99.8
A(N-Pt-Cl)	(90.234-90.429) deg.	88.9	81.7	82.1
A(Cl-Pt-Cl)	89.703 deg.	91.9	96.4	96.1
A(H-N-H)	(109.248-109.487) deg.	107	110	110
A(H-N-Pt)	(112.607-109.882) deg.	111	109	109

Table 3 illustrates the calculated values of the high occupied molecular orbital energy E_{HOMO}, the low unoccupied molecular orbital E_{LUMO} energy and the energy gap E_{gap} in eV of the cis-platin. We showed a good agreement in a comparison with ref.[17] and this an indication to a suitable method was used in present work, where a wide separation was obtained between the valence and conduction bands as noted in fig.2. Fig.3 illustrated the 3-D distribution of the HOMO and LUMO energies due to the linear combination of atomic orbitals for all atoms in the compound to construct the molecular orbitals, where the great contribution is from outer electrons in the platinum metal with few contributions from the p-orbitals of the ligands, the green color represents the positive charges and the red color represents the negative charges. From our calculations, the E_{gap} is 4.517 eV in which the cis-platin has insulating behavior. The electrostatic potential ESP in fig.4 shows the charges are highly dragged towards the ligands chlorine atoms according to their largely electronegativity in comparison with the other atoms in the compound.

Table.3: The HOMO, LUMO energies and energy gap of the cis-platin.

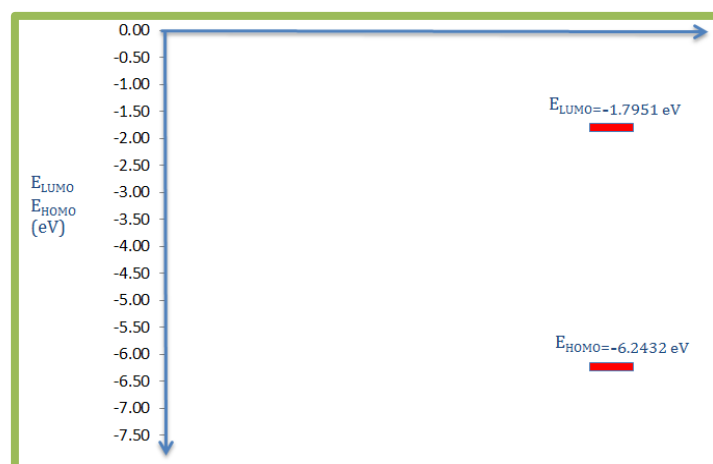| Method	E_{HOMO} (eV)	E_{LUMO} (eV)	Egap (eV)
Present work	-6.2432	-1.7951	4.4481
Reference [17]	-6.313	-1.796	4.517

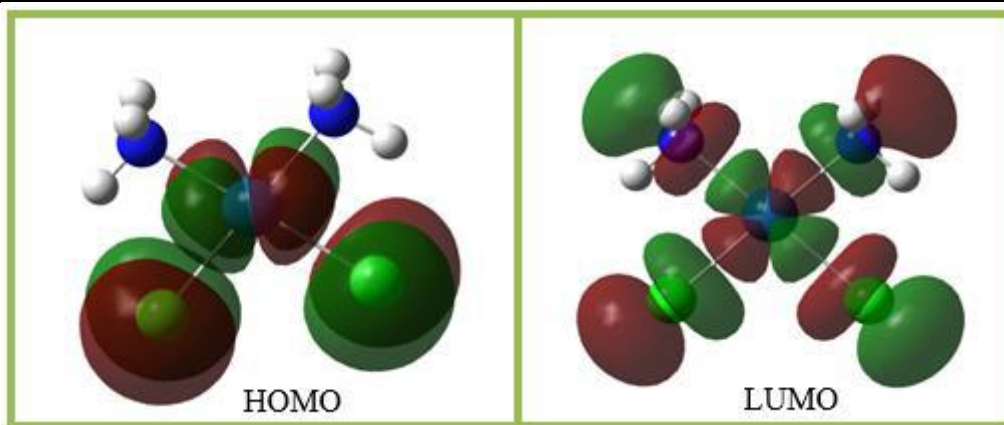*Fig.2: The LUMO-HOMO gap of the cis-platin.*

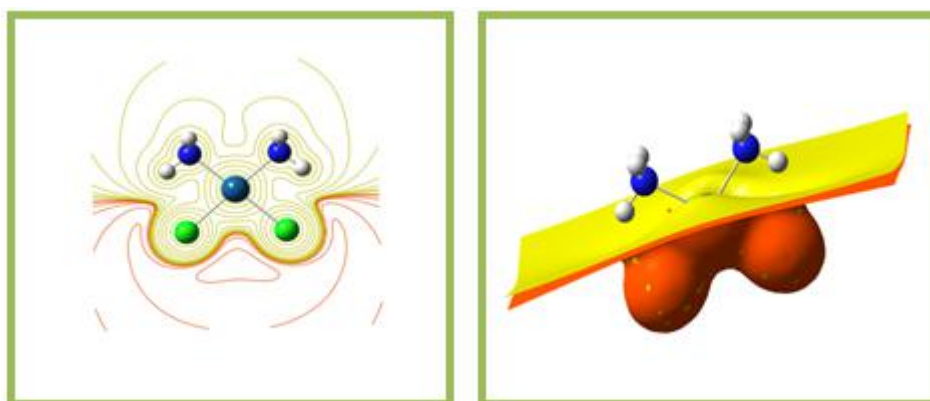*Fig. 3: The 3-D distribution of HOMO and LUMO of the cis-platin.*

Fig. 4: The ESP distribution of the cis-platin.

Some of electronic properties of cis-platin are listed in Table 4. A good value was obtained for virial ratio (- V/T = 2.0770) of the compound without any imaginary frequency in which refers to good relaxation obtained for the studied structure. The calculated values of ionization energy I_E and electron affinity E_A showed the cis-platin has very low ability to donating/ accepting an electron to becomes cation/anion, these results are correspond to the large value of energy gap of the compound and it has insulating behavior. The results showed the cis-platin has low value of electronic softness S, so, the calculated values of electronegativity X, electrochemical hardness H, chemical potential μ and electrophilic index ω in this work using SDD basis sets are in good agreement with those in ref.[17]. Above results declare the cis-platin needs to high excitation energy to electron transfer or to accepting an electron from the surrounding species.

Table.4: Some electronic variables of the cis-platin.

Property	The present work (DFT-B3LYP/SDD)	Reference [17] (DFT-B3PW91/LANL2DZ)
E_T (a. u)	-1152.9958	----
$\frac{-V}{T}$	2.0770	----
I_E(eV)	6.2432	----
E_A(eV)	1.7951	----
(XeV)	4.0192	4.054
H(eV)	2.2240	2.258
S(eV)$^{-1}$	0.2248	----
μ (eV)	-4.0192	-4.054
ω(eV)	3.6315	3.639

IV.   CONCLUSION

From the results of the structural and electronic properties of the cis-platin using SDD/DFT, one can conclude the following:

1. the calculated values of bonds and the angles are in good agreement with other studies.
2. A wide gap was obtained between the valence and conduction bands, means, cis-platin has insulating behavior. The great contribution for constructing the molecular orbitals is due to the outer electrons in the platinum metal with few contributions from the p-orbitals of the ligands.
3. The charges are highly dragged towards the ligands chlorine atoms and the ESP was distributed due to the coordination of all atoms in the compound.
4. A good relax was obtained for the studied structure via the calculated value of virial ratio without any imaginary frequency.
5. The cis-platin has very low ability to donating or accepting an electron to becomes cation or anion.
6. The cis-platin has low value of electronic softness and it needs high excitation energy to electron transfer or to accepting an electron from the surrounding species.

V.   ACKNOWLEDGEMENTS

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