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ORIGINAL RESEARCH PAPER

Solvent influence on the interaction of *cis*-$PtCl_2(NH_3)_2$ complex and graphene: A theoretical study

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ABSTRACT

In this study the interaction of *cis*-$PtCl_2(NH_3)_2$ complex and graphene were investigated with MPW1PW91 method in gas and solvent phases. The solvent effect was examined by the self-consistent reaction field theory (SCRF) based on Polarizable Continuum Model (PCM). The selected solvents were chloroform, chlorobenzene, bromoethane, dimethyldisulfide, and dichloroethane. The solvent effect on the frontier orbital energy and HOMO-LUMO gap were studied. The characterization of the interaction between two fragments was clarified with energy decomposition analysis (EDA). Pt-C(Graphene) and $H(NH_3)$...C(Garaphen) interactions in the graphene … *cis*-$PtCl_2(NH_3)_2$ complex were analyzed using quantum theory of atoms in molecules analysis (QTAIM).

Keywords: *Cis-$PtCl_2(NH_3)_2$ Complex; Energy Decomposition Analysis (EDA); Graphene, Polarizable Continuum Model (PCM); Quantum Theory of Atoms In Molecules Analysis (QTAIM), Solvent Effect*

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INTRODUCTION

Graphene has a two dimensional crystal without volume and with one surface, that increase the influence of surface dopants and hold new magnetic and electronic properties. In fact, the single atomic plane of graphite is regarded as graphene. The synthesis of garaphene initiated a novel revolution in nanotechnology [1]. The special two-dimensional structure, noticeable mechanical, electrical and thermal properties of graphene exited many investigations [2-5]. Accessible production and economical, a large surface for adsorption of hydrogen are the advantages of graphene. Also, theoretical researches excited attempts for illustration of graphene properties [6-12]. Also, the organometallic chemistry of graphitic compounds has excessive probable for the understanding of novel materials and η^6-complexation reactions of chromium with numerous forms of graphene, graphite and carbon nanotubes have been reported [13].

Cisplatin is used extensively as anticancer drug [14] which has been predominantly fruitful in treating small cell lung, testicular, ovarian, neck tumors, and head [15]. Then the finding of this drug [16, 17] much growth has been made in comprehending its manner of achievement and numerous facts of the mechanism of its antitumor activity are currently perfect [18, 19]. The employment of platinum-based drugs in the clinic has their serious side effects (for example: vomiting. nausea, myelosuppression, neurotoxicity, and ototoxicity) [20]. Consequently, growth of novel delivery systems that can decrease the severity of the drugs' side-effects is valuable [21, 22]. For instance, a cisplatin slow-release hydrogel drug delivery system based on a formulation of the

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macrocycle cucurbit[7]uril, gelatin and polyvinyl alcohol has been reported [23]. Furthermore, theoretical studied have been reported about the structure, bonding, properties and action mechanism of the drugs [24-28].

In their attempts to progress a drug delivery system, numerous researchers have assessed the capability of carbon nanotubes (CNT) and nanocages [29]. Drug delivery can be achieved either through filling the inner space of the tubes with porphyrins [30], metals [31], and biomolecules [32] or by attaching proteins and compounds (via a specific adsorption or covalent bond) on their external surface. In other research, loading of a phenanthroline-based Platinum(II) complex onto the surface of a carbon nanotube via π–π Stacking has been studied [33].

Theoretical calculations using the DFT formalism are very general in order to realize thorough electronic structures of complicated coordination compounds from a microscopic viewpoint [26, 34-50]. The current calculations did not contain micro-solvent effect of solvent molecules with solute cations as solvent molecules were not used explicitly.

To realize the solvation effect on the interaction of *cis*-$PtCl_2(NH_3)_2$ complex and graphene in solution more quantitatively from the microscopic viewpoint, more sophisticated calculations are essential such as QM/MM (quantum mechanics/molecular mechanics) approach.

The basis goal of this investigation was to reveal the interaction of *cis*-$PtCl_2(NH_3)_2$ complex and garaphene by the quantum mechanics method in gas and solvent phases. The stability, dipole moment, structural parameters, of this complex was illustrated Moreover, EDA and QTAIM methods were used for illustration of the interactions in this complex.

COMPUTATIONAL METHOD

All calculations were carried out with the Gaussian 09 suite of program [51]. The calculations of systems contain main group elements described by the standard 6-311G(d,p) basis set [52-55]. Calculation related to Pt element was performed using the element standard Def2-TZVPPD basis set [56].The pseudo-potential effective core potential (ECP) using the Def2-TZVPPD basis set, was applied to describe Pt [57]. The Modified Perdew-Wang Exchange and Correlation (MPW1PW91) method was employed for the purpose of geometry optimization[58]. Harmonic vibrational frequencies were calculated to verify that the optimization structures have no imaginary frequency.

For the solvation effect study, the structure of complex was reoptimized in selected solvents by a self-consistent reaction field (SCRF) approach, in particular using the polarizable continuum model (PCM) [59].

The bonding interactions between the graphyne and *cis*-$PtCl_2(NH_3)_2$ complex fragment were evaluated considering energy decomposition analysis (EDA) in the Multiwfn 3.3.5 software package [60]. Between the two fragments, the instantaneous interaction energy (E_{int}) was calculated as:

$$\mathbf{\Delta E_{int} = \Delta E_{polar} + \Delta E_{els} + \Delta E_{Ex}}$$

Where E_{polar} is the electron density polarization term (the induction term) calculated by subtracting E (SCF last) from E (SCF 1st). E_{els} and E_{Ex} are the electrostatic interaction and the exchange repulsion terms, respectively.

The Multiwfn 3.3.9 software package was also used for the topological analysis of electron density [61].

RESULTS AND DISCUSSION

Energetic aspect

Fig. 1 present the optimized structure of *cis*-$Pt(NH_3)_2Cl_2$…Graphene complex in gas and solution phases. To evaluate the interaction of *cis*-$Pt(NH_3)_2Cl_2$ and graphene, we have selected

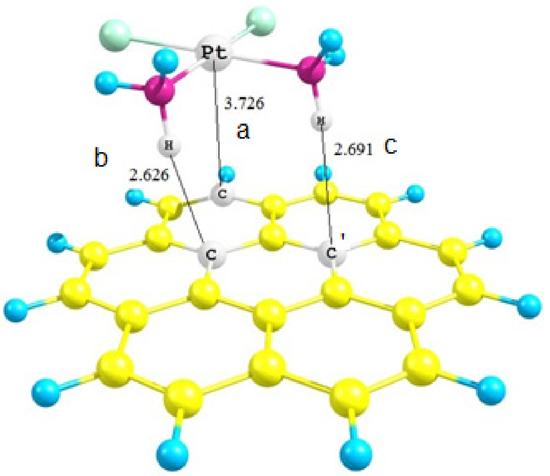

Fig. 1. The structure of *cis*-$Pt(NH_3)_2Cl_2$…Graphene complex and selected interatomic distances in gas phase.

coronene cluster ($C_{24}H_{12}$) as a large planar polycyclic aromatic hydrocarbons (PAH) that is accepted to be a proper model for theoretical examination on graphene [62].It can be observed, square planar of *cis*-$Pt(NH_3)_2Cl_2$ complex is oriented approximately parallel with graphene layer.

The absolute energy and solvation energy values of the studied complex in gas and various solvent are gathered in Table 1. The negative value of solvation energy values reveals the more stability of *cis*-$Pt(NH_3)_2Cl_2$…Graphene complex in solution in compared to gas phase. The larger negative values of solvation energy values in more polar solvent illustrates the more stability of this complex in the more polar solvent. It can be observed a good linear correlation between solvation energy values and dielectric constant values of solvents (Fig. 2):

$$E_{solv} = -0.8799\ \varepsilon - 14.908; \quad R^2 = 0.9648$$

Dipole moment

Dipole moment values of the of *cis*-$Pt(NH_3)_2Cl_2$…Graphene complex are listed in Table 1. The larger dipole moment value of various solvents attribute to the additional dipole moment induced by the solvents. There is a good linear relationship between solvation energy values and dipole moment in different solvents (Fig. 3):

$$E_{solv} = -4.3868\ \mu + 51.641; \quad R^2 = 0.9163$$

Energy decomposition analysis (EDA)

The chemical bond nature between the graphene fragment with *cis*-$Pt(NH_3)_2Cl_2$ complex is explored using an energy decomposition analysis (EDA). Results of these calculations reveal the interaction energy value of graphene fragment with *cis*-$Pt(NH_3)_2Cl_2$ complex is -7.57 kcal/mol, in gas. The interaction energy values in different solvent are listed in Table 1.The negative total energy of interaction values between graphene fragment with *cis*-$Pt(NH_3)_2Cl_2$ complex show interactions between two fragments. It can be seen, the interaction strength between two fragments is stronger in gas phase in compared to solution phase.

Structural parameters

Fig. 3 presents the shortest distances of Pt … C(Graphene) and H(NH_3) …. C(Garaphene) in the *cis*-$Pt(NH_3)_2Cl_2$…Graphene complex in gas.

Table 1. Absolute energy (E, Hartree), solvation energy (E_{solv}, kcal/mol), total dipole moment (Debye), interaction energy (kcal/mol), and Pt…C (a), H..C (b,c) distances (in Å) for *cis*-$Pt(NH_3)_2Cl_2$ … graphene complex in gas and solution phases.

	ε	E	E_{solv}	μ	E_{int}	a	b	c
gas	-	-2075.034	-	10.95	-7.57	3.726	2.626	2.691
Chloroform	4.71	-2075.064	-18.55	15.91	-2.74	4.241	2.777	3.274
Chlorobenzene	5.70	-2075.067	-20.23	16.62	-3.30	4.329	3.590	3.747
THF	7.43	-2075.069	-21.92	16.83	-2.94	4.356	3.637	3.792
BromoEthane	9.01	-2075.071	-22.96	16.97	-2.73	4.356	3.639	3.792
DiMethylDiSulfide	9.60	-2075.072	-23.27	17.00	-2.66	4.357	3.639	3.792
DiChloroEthane	10.13	-2075.072	-23.51	17.04	-2.61	4.357	3.639	3.792

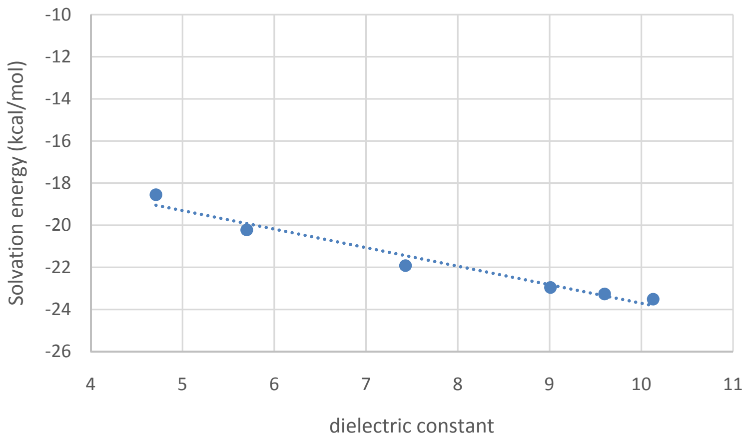

Fig. 2. Linear correlation between solvation energy and dielectric of solvents for *cis*-$Pt(NH_3)_2Cl_2$…Graphene complex in various solvents.

These values for this complex in various solvents are gathered in Table 1. It can be seen, these distances are longer in solution phase than gas phase. As a result, these distances predict stronger interaction between *cis*-Pt$(NH_3)_2Cl_2$ and graphene in gas phase. These distances are compatible with interaction energy values of the complex in two phases.

Molecular orbital analysis

Frontier orbital energy values and HOMO-LUMO gap of *cis*-Pt$(NH_3)_2Cl_2$…Graphene complex in the and selected solvents are shown in Table 2. The HOMO and LUMO energy values of the *cis*-Pt$(NH_3)_2Cl_2$…Graphene complex are -6.22 and -2.05 eV in gas. The comparison of these values with corresponding values in solvent system show that HOMO are stabilized in solution phase. In contrast, the stability of LUMO decrease in solution phase. The HOMO-LUMO gap values in the studied complex are 4.17 eV in gas. It can be observed HOMO-LUMO gap increase in solution phase. This means that electron transfer between frontier orbitals (HOMO→LUMO) is easy in gas phase in compared to solution phase. The increase in the dielectric constant of the solvent and possible interactions between the solute and solvent molecules causes to increase the energy gap.

Plots of frontier orbital in this complex are presented in Fig. 4. It can be observed, only *cis*-Pt$(NH_3)_2Cl_2$ fragment contributes in HOMO of complex. In contrast, only graphene fragment contributes in LUMO complex.

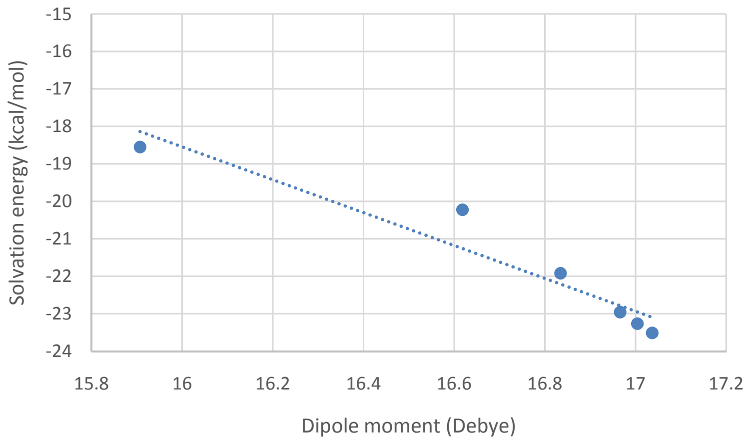

Fig. 3. Linear correlation between solvation energy and dipole moment values for *cis*-Pt$(NH_3)_2Cl_2$…Graphene complex in various solvents.

Table 2. Frontier orbital energy and HOMO-LUMO gap (in eV) for *cis*-Pt$(NH_3)_2Cl_2$ … graphene complex in gas and solution phases.

	E(HOMO)	E(LUMO)	HOMO-LUMO gap
gas	-6.22	-2.05	4.17
Chloroform	-6.30	-1.98	4.32
Chlorobenzene	-6.29	-1.96	4.33
THF	-6.27	-1.94	4.32
BromoEthane	-6.26	-1.93	4.32
DiMethylDiSulfide	-6.25	-1.93	4.32
DiChloroEthane	-6.25	-1.93	4.32

Table 3. Thermodynamic parameters for *cis*-Pt$(NH_3)_2Cl_2$ … graphene complex in gas and solution phases.

	G(a.u)	H(a.u)	G_{sol}(kcal/mol)	H_{sol}(kcal/mol)
gas	-2074.729018	-2074.644085	-	-
Chloroform	-2074.759172	-2074.672917	-18.92	-18.09
Chlorobenzene	-2074.759921	-2074.675410	-19.39	-19.66
THF	-2074.761939	-2074.678020	-20.66	-21.29
BromoEthane	-2074.763517	-2074.679650	-21.65	-22.32
DiMethylDiSulfide	-2074.763985	-2074.680132	-21.94	-22.62
DiChloroEthane	-2074.764372	-2074.680519	-22.19	-22.86

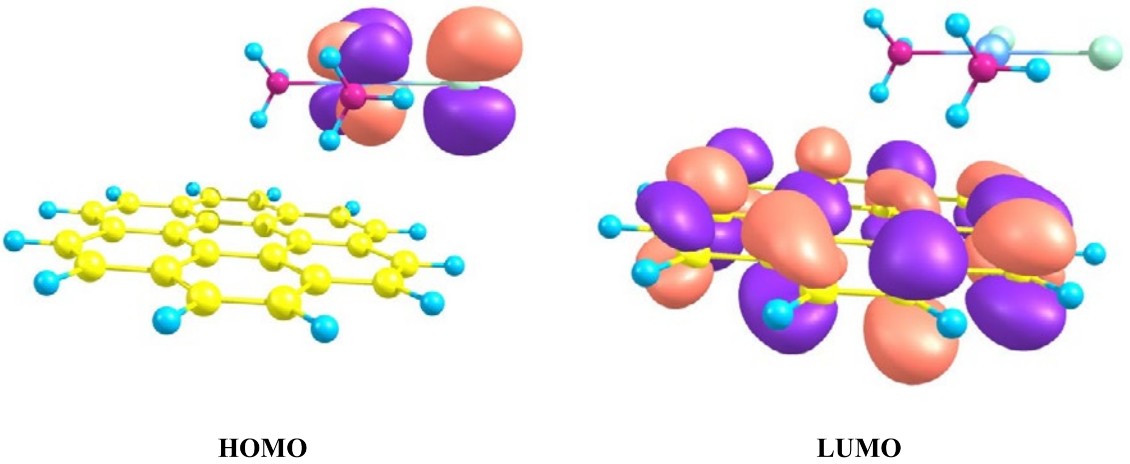

Fig. 4. Plots of frontier orbitals for optimized *cis*-$Pt(NH_3)_2Cl_2$…Graphene complex in gas phase.

Table 4. QTAIM results of Pt-C(garaphene) and $H(NH_3)$-C(garaphene) interactions in *cis*-$Pt(NH_3)_2Cl_2$ … graphene complex.

	ρ	$\nabla^2\rho$	G	H	V
Pt-C	0.00590	0.01585	0.00337	0.00059	-0.00277
H-C	0.00773	0.02348	0.00482	0.00105	-0.00377
H-C'	0.00697	0.02142	0.00436	0.00100	-0.00336

Thermodynamic parameters

The absolute free energy and enthalpy values of the *cis*-$Pt(NH_3)_2Cl_2$…Graphene are summarized in Table 4. The solvation free energy and enthalpy values are evaluated as:

$$\Delta X_{solvation} = X_{solv} - X_{gas};\ X = G, H$$

It can be found, increasing the polarity of solvent resulted in decreased G_{solv} and H_{solv} values of the investigated complex. Additionally, G_{solv} and H_{solv} values show good relationships with the dielectric constant values:

$$G_{solv} = -0.6243\ \varepsilon - 15.945;\quad R^2 = 0.9966$$
$$H_{solv} = -0.8496\ \varepsilon - 14.545;\quad R^2 = 0.9682$$

Quantum theory of atoms in molecules (QTAIM) analysis

Understanding of the chemical and physical properties of molecules is possible by using Quantum theory of atoms in molecules (QTAIM) analysis [63-67]. Therefore, we study topological parameters of the studied complexes. QTAIM analysis reveals bond critical point (BCP) between Pt and $H(NH_3)$ with $C_{graphyne}$ atoms. The results of these analysis for Pt-$C_{garaphyne}$ and H-C bonds are gathered in Table 4. It can be found, the total electron density is larger on the BCP of the H-C bonds in compared to Pt-C bond.

It is obvious that Pt-C bonds are polar, as is the situation regularly in the coordinate bonds. This is detected in the positive Laplacian values, which illustrates charge depletion in the bond critical points. Laplacian of electron density of in bond critical point (BCP) of Pt-$C_{graphyne}$ and H-C bonds bonds in the basis of the QTAIM calculations are listed in Table 4. As seen, $\nabla^2\rho$ values are positive at their corresponding BCP. These values are expected for closed-shell interactions.

Energy density of in bond critical point (BCP) of Pt-C(graphene) and H-C interactions in the basis of the QTAIM calculations are reported in Table 4 the total energy density (H) is defined as:

$$H = G + V$$

In this equation G and V are Lagrangian kinetic energy and Virial energy density, respectively. QTAIM results reveal V values are negative. This negative value of H is compatible with shared interactions in Pt-$C_{graphyne}$ and H-C bonds bonds. Consequently, these results are compatible with preceding findings for the M–C bonds in organometallic complexes [68] and transition metal carbonyl clusters [69], where the characteristics of the metal–ligand bonding is intermediate between closed-shell and shared interactions. On the other hand, the positive $\nabla^2\rho(r)$ and H(r) topological descriptors and -G(r)/V(r) descriptor is also greater than one at BCP of C-H, implying that this interaction should be classified as weak and non-covalent.

CONCLUSION

Theoretical study on interaction of *cis*-Pt$(NH_3)_2Cl_2$ with graphene in gas phase and selected solvents was revealed :

1. Negative value solvation energy of the between *cis*-Pt$(NH_3)_2Cl_2$ …. graphene complex signifies the more stability of the complex in solution in comparison to gas phase.

2. There are good linear correlations between E_{sol} with dipole moment and dielectric constant values.

3. EDA and structural parameters predict stronger interaction between *cis*-Pt$(NH_3)_2Cl_2$ and graphene in gas phase.

4. *cis*-Pt$(NH_3)_2Cl_2$ and graphene fragments contribute in HOMO and LUMO of complex, respectively.

5. In the basis of QTAIM analysis, the characteristics of the Pt…C(Graphene) and H(NH_3)… C(Graphene) interactions was intermediate between closed-shell and shared interactions.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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