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Full Length Research Paper

Ab-initio study of the ground state structure and properties of Fe^{+2} $(thymine)_2$ $(H_2O)_2$ complex

D. De, S. Dalai and B. R. De*

Department of Chemistry and Chemical Technology, Vidyasagar University, Midnapore, 721102, India.

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Hartree-Fock calculations with 6-31G (d) basis set have been done in the gas phase on Fe^{+2} $(thymine)_2$ $(H_2O)_2$ complex with complete geometry optimization. Stable structure for the complex has been found. Single point water phase calculation (PCM) has also been done which shows that the complex is more stable in water implying its physiological action for the removal of excess hazardous Fe^{+2} from the body. Selected optimized geometrical parameters, charge densities on selected atoms have been reported. HOMO-LUMO energies and structures are shown. The LUMO structure shows that the Fe^{+2} play the key role of the complex. The study may help in the new drug discovery.

Key words: Gaussian, gas phase, water phase, Hartree-Fock, charge density.

INTRODUCTION

The specific interactions between the purine and pyrimidine bases are one of the corner stones of the molecular biology (Saengen, 1984; Jeffrey, 1991; Huysken, 1991; Chandra, 1998). It is well known (Snustad et al., 2003) that hemoglobin provides an excellent illustration of quaternary structure. Each unit of hemoglobin is composed of α2 and β2 chains. Hemoglobin is normally formed in the body. If any malfunctioning occurs in its formation (Huheey, 2004) due to genetic or any other causes, several diseases like thalasemia, sickle cell anemia, excess Fe^{+2} accumulations, etc., appear in the body. If this excess Fe^{+2} be removed by complexation with either of the purine or pyrimidine bases, then there may be some possibilities of curing the mentioned diseases. Previously, chelate therapy was used to treat excessive quantities of copper in the body (Huheey, 2004). Keeping this view in mind, the present work has been undertaken to examine theoretically, the reaction between Fe^{+2} and thymine as a case study.

COMPUTATIONAL DETAILS

Complete geometry optimizations for Fe^{+2} $(thymine)_2$ $(H_2O)_2$ complex were done in the gas phase by Hartree-Fock method with 6-31G (d) basis set using Gaussian 03W program (Frisch et al, 2004). Actually, this optimization gives the most stable conformation of the system studied. Moreover for first hand information Hartree-Fock method with 6-31G (d) basis set is sufficient in comparison to more popular DFT method which requires much more computation time. Single point water phase calculations at the gas phase equilibrium geometry were also done using the same basis set by polarizable continuum model (PCM) approach at HF level. Here also optimization in water phase calculation is not done because of computation time problem.

RESULTS AND DISCUSSION

Equilibrium geometry of the studied complex with the numbering scheme of the atoms is shown in Figure 1a. The single point water phase calculations using the gas phase equilibrium geometry is shown in Figure 1a, b. The significant variations in these figures are indicated by some selective geometrical parameters given in Table 3. Table 1 reports in the gas phase, the computed total energy (hartree), dipole moment (debye) and ΔE (HOMO-LUMO gap) (hartree), at the equilibrium geometry of the complex along with single point water phase data. Table 2 summarizes the computed net Mulliken charge on the selected hetero atoms of the complex at the equilibrium geometry of the complex in the gas phase including the single point water phase calculations. The hetero atoms are assumed to play the key role for the physiological drug action because these are the most negative centres of the complex. The drug action is assumed to take place through chemical attack.

*Corresponding author. E-mail: brdranjan@yahoo.com

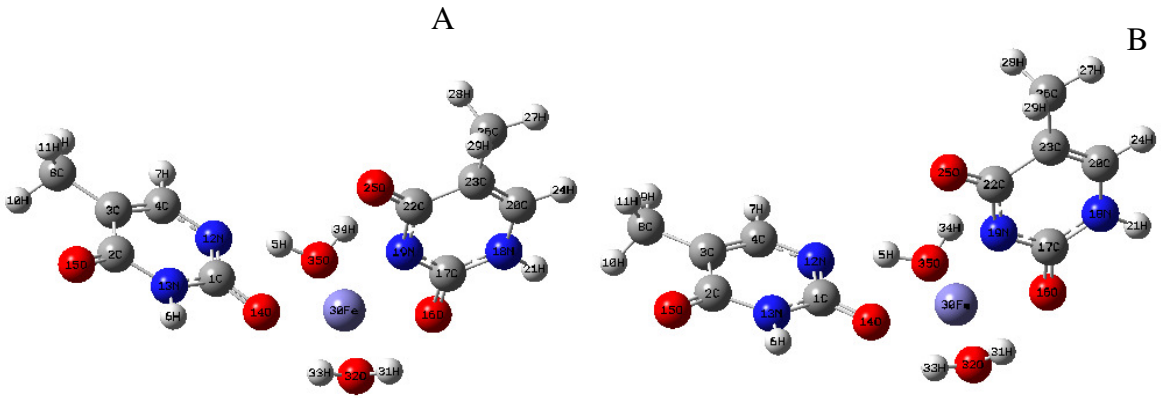

Figure 1. a) Optimized structure of Fe^{+2} $(Thymine)_2$ $(H_2O)_2$ complex in gas phase; b) Single point structure of Fe^{+2} $(Thymine)_2$ $(H_2O)_2$ complex in water phase.

Table 1. Computed total energies (hartree) dipole moments (debye), HOMO, LUMO energies (hartree) and ΔE (HOMO-LUMO gap)(hartree) at the equilibrium geometry of the ground state of Fe^{+2} (thymine $)_2$ $(H_2O)_2$ complex.

Complex in	Total energy	Dipole moment	HOMO	LUMO	ΔE(HOMO-LUMO gap)
Gas phase	-2316.1928	9.9096	-0.2994	0.0971	0.3965
Water phase	-2316.2605	13.1724	-0.3120	0.1133	0.4253

1 hatree = 627.5095 kcal(mole)-1 = 27.2116 eV.

Table 2. Computed net Mullikan charge/electron density on the selected atoms of Fe^{+2} $(thymine)_2$ $(H_2O)_2$ complex at the equilibrium ground state and single point data in water phase.

Atoms	Complex in gas phase	Complex in water phase
H_5	0.5592	0.5585
N_{12}	-0.8485	-0.8473
N_{13}	-0.9034	-0.9090
O_{14}	-0.9069	-0.8916
O_{15}	-0.6212	-0.6919
O_{16}	-0.8066	-0.8402
N_{18}	-0.8667	-0.8704
N_{19}	-0.9982	-0.9973
O_{25}	-0.6047	-0.6922
Fe_{30}	1.3958	1.4030
H_{31}	0.4945	0.5294
O_{32}	-0.9302	-0.9727
H_{33}	0.5128	0.5327
H_{34}	0.4818	0.5213
O_{35}	-0.9952	-1.0231

From Table 1, it is seen that the complex is highly stable in the gas phase at the equilibrium geometry. The stability is increased in the water phase because the total energy of the system in this phase is more negative than in gas phase. Mulliken population analysis is not unique; still it is very important to provide an idea of electron density distribution in a molecular system. The calculated dipole moment reflects an overall charge/electron density distribution in a molecular system. From Table 1 it is seen that the dipole moment of the complex in water phase is 1.5 times greater than that in gas phase as it is expected [polar complex in polar solvent]. The HOMO is more stabilized in water phase but the LUMO is little bit destabilized than the gas phase.

From Table 2, it is seen that the Fe^{+2} (in its closed shell configuration) ion receives 0.6042 and 0.5970 e amount

Table 3. Computed values of some selected geometrical parameters (length in A^0) at the equilibrium ground state of Fe^{+2} $(Thymine)_2$ $(H_2O)_2$ complex.

Atoms	Length	Atoms	length	Atoms	length
C_1-N_{12}	1.3081	O_{16}-Fe_{30}	2.0822	N_{18}-C_{20}	1.3858
C_1-N_{13}	1.3590	C_{17}-Fe_{30}	2.4406	N_{19}-C_{22}	1.3737
C_1-O_{14}	1.2662	N_{19}-Fe_{30}	2.0784	H_{31}-O_{32}	0.9496
C_2-N_{13}	1.3884	Fe_{30}-O_{32}	2.0673	N_{18}-H_{21}	0.9948
C_2-O_{15}	1.2014	Fe_{30}-O_{35}	2.0204	Fe_{30}-N_{12}	3.3400
C_4-N_{12}	1.3662	O_{32}-H_{33}	0.9532	H_5-N_{12}	1.7439
H_5-O_{35}	0.9823	H_{34}-O_{35}	0.9479	H_{33}-O_{14}	2.2501
H_6-N_{13}	0.9969	C_{17}-N_{18}	1.3490	H_{34}-N_{19}	3.1213
O_{14}-Fe_{30}	1.9790	C_{17}-N_{19}	1.3248	H_{31}-N_{19}	2.9124
O_{16}-C_{17}	1.2483	C_{22}-O_{25}	1.2002		

Table 3 (Contd). Computed values of some selected geometrical parameters (angle in degree) at the equilibrium ground state of Fe^{+2} $(Thymine)_2$ $(H_2O)_2$ complex.

Atoms	Angle in degree	Atoms	Angle in degree
O_{14}- Fe $_{30}$-C_{17}	149.32	C_1-O_{14}- Fe $_{30}$-C_{17}	86.15
O_{14}- Fe $_{30}$-N_{19}	116.65	C_1-O_{14}- Fe $_{30}$- N $_{19}$	81.22
O_{14}- Fe $_{30}$-O_{32}	81.14	C_1-O_{14}- Fe $_{30}$-O_{32}	171.22
O_{14}- Fe $_{30}$-O_{35}	92.70	C_1-O_{14}- Fe $_{30}$-O_{35}	-20.88
O_{16}- Fe $_{30}$- N $_{19}$	63.60	O_{14}- Fe $_{30}$-O_{32}-H_{31}	-129.93
O_{16}- Fe $_{30}$-O_{32}	93.71	O_{16}- Fe $_{30}$-O_{32}-H_{33}	167.66
O_{16}- Fe $_{30}$-O_{35}	92.28	C_{17}- Fe $_{30}$-O_{32}-H_{33}	136.84
N $_{19}$- Fe $_{30}$-O_{32}	93.95	N $_{19}$- Fe $_{30}$-O_{32}-H_{31}	-13.55
N $_{19}$- Fe $_{30}$-O_{35}	99.56	O_{35}- Fe $_{30}$-O_{32}-H_{31}	166.38
Fe $_{30}$-O_{32}-H_{33}	103.19	O_{16}-C_{17}-N_{18}-H_{21}	0.19
H_{31}-O_{32}-H_{33}	107.69	O_{25}-C_{22}-C_{23}-C_{26}	-1.09
O_{14}-C_1-N_{12}-C_4	179.55	O_{14}- Fe $_{30}$-O_{35}-H_5	15.59
N_{12}-C_1-O_{14}- Fe $_{30}$	12.27	O_{16}- Fe $_{30}$-O_{35}-H_5	-165.67
N_{13}-C_1-O_{14}- Fe $_{30}$	-168.64	O_{32}- Fe $_{30}$-O_{35}-H_{34}	-158.67
C_3-C_2-N_{13}-C_1	0.11	O_{32}- Fe $_{30}$-O_{35}-H_5	77.83
O_{15}-C_2-N_{13}-H_6	-0.85		

of charge in gas and water phase respectively from two thymine ligands and two water ligands. In almost all the hetero atoms, the charge densities in gas phase is a little less than that in the water phase implying that in water phase, the negative centers become more effective.

HOMO and LUMO structures of the complex both in gas phase and single point water phase are shown in Figures 2a, b, and 3a, b, respectively. The significance of the figures is that complete geometry of the complex is seen which is not reflected from the selected geometrical parameters shown in Table 3. The LUMO structure shows that Fe^{+2} ion plays the key role of the complex both in gas phase and water phase which is also supported from figures. Table 3 shows some selected geometrical parameters of the complex in the gas phase particularly the metal containing zone and other heteroatom containing zone. From Table 3, it is seen that Fe^{+2} containing zones are non planar and this part of the complex is out of plane from both the thymine ligands and two H2O ligands also. Fe –O (35) and Fe-O (32) distances are 2.0204 A0 and 2.0673A0 respectively. Fe-O (14) and Fe-O (16) distances are 1.9796 A0 and 2.0822A0, respectively. Fe-N (12) and Fe-N (19) distances are 3.3400 A0 and 2.0783 A0, respectively. The most stable conformation of the system favors such geometrical parameters.

Conclusions

From the present theoretical study, it is found that the Fe^{+2} $(thymine)_2$ $(H_2O)_2$ complex is a stable complex both

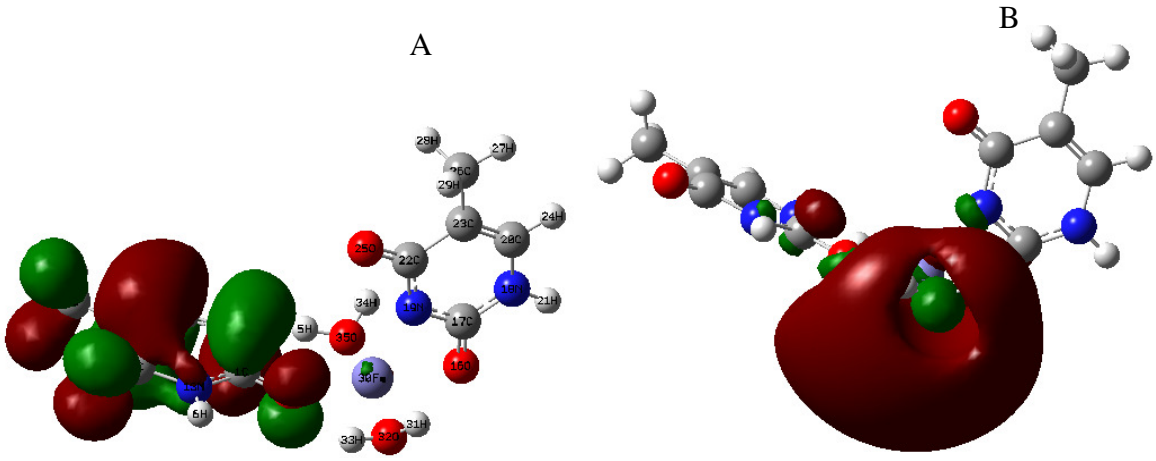

Figure 2. (a) HOMO structure of Fe^{+2} $(Thymine)_2$ $(H_2O)_2$ complex in gas phase; b) LUMO structure of Fe^{+2} $(Thymine)_2$ $(H_2O)_2$ complex in gas phase.

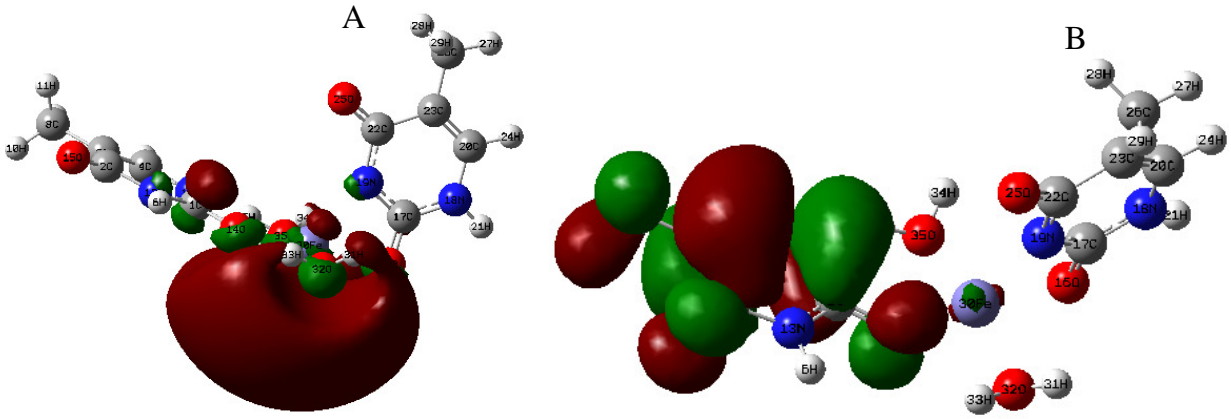

Figure 3. a) LUMO structure of Fe^{+2} $(thymine)_2$ $(H_2O)_2$ complex in water phase. (b) HOMO structure of Fe^{+2} $(thymine)_2$ $(H_2O)_2$ complex in water phase.

in gas phase and in water phase (single point calculation by polarisable continuum model- PCM). This first hand information of the title complex signifies its physiological importance for the removal of excess Fe^{+2} from the body. The LUMO structure shows that Fe^{+2} ion plays the key role of the complex both in gas phase and water phase. The present study may help in the discovery of new drugs.

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